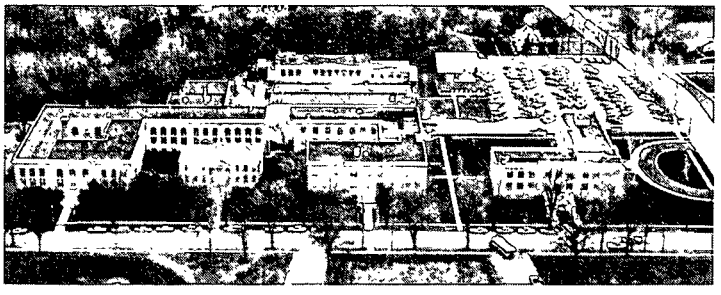


THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

STATUS REPORTS

To The

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

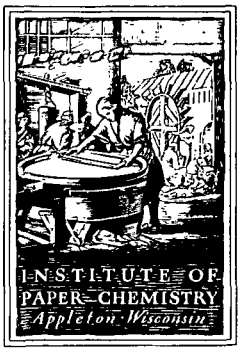
October 22-23, 1985
The Institute of Paper Chemistry
Continuing Education Center
Appleton, Wisconsin

NOTICE & DISCLAIMER

The Institute of Paper Chemistry (IPC) has provided a high standard of professional service and has exerted its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for the internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPC does not recommend particular products, procedures, materials, or services. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPC or its employees and agents have any obligation or liability for damages, including, but not limited to, consequential damages, arising out of or in connection with any company's use of, or inability to use, the reported information. IPC provides no warranty or guaranty of results.



THE INSTITUTE OF PAPER CHEMISTRY
Post Office Box 1039
Appleton, Wisconsin 54912
Phone: 414/734-9251
Telex: 469289

September 30, 1985

TO: MEMBERS OF PAPER PROPERTIES AND USES PROJECT ADVISORY COMMITTEE

Attached for your review are the Status Reports for the Projects to be discussed at the Paper Properties and Uses PAC meeting scheduled for October 22-23, 1985, in Appleton. A meeting agenda can be found inside this booklet.

For those of you staying at the Continuing Education Center, the attached pink card gives the combination to the front door so that you can gain entrance if you arrive after the doors are locked. Room schedules are posted in the lobby. If you have not made your reservations yet and wish to stay at CEC, please advise Ms. Burton at 414/738-3259.

We look forward to seeing you on October 22. Best regards.

Sincerely yours,

Gary Baum/sb

Gary A. Baum
Director
Paper Materials Division

GAB/sb
Enclosure

TABLE OF CONTENTS

	Page
AGENDA	ii
COMMITTEE ROSTER	iv
Project 3469 -- Compressive Strength	2
Project 3571 -- Board Properties and Performance	24
Project 3500 -- Combined Stress and Failure Processes	50
Project 3467 -- Process, Properties, Product Relationships	72
Project 3527 -- Measurement of Fiber Properties and Fiber-to-Fiber Bonding	105
Project 3526 -- Fundamentals of Internal Strength Enhancement	113
Project 3332 -- On-line Measurement of Paper Mechanical Properties	145
Project 3566 -- Strong, Intact, High Yield Fibers	168

MEETING AGENDA

PAPER PROPERTIES AND USES
PROJECT ADVISORY COMMITTEE

October 22-23, 1985
The Institute of Paper Chemistry
Continuing Education Center
Appleton, WI

Tuesday, October 22

8:30 am	Welcome/Introductions	G. Homan/G. Baum
8:45	PROJECT OVERVIEW	G. Baum
9:15	PROJECT REVIEW	
	Compressive Strength	B. Whitsitt/J. Waterhouse
10:00	COFFEE BREAK	
10:30	PROJECT REVIEWS	
	Board Properties and Performance	B. Whitsitt/B. Halcomb
	Combined Stress & Failure Processes	J. Waterhouse
	Student Research	L. Charles
12:00	LUNCH	
1:00	PROJECT REVIEWS	
	Process, Properties, Product Relationships	G. Baum/C. Habeger
	Student Research	B. Berger
	Student Research	W. Westervelt
	Student Research	D. Waterman
	Measurement of Fiber Properties and Fiber-Fiber Bonding	K. Hardacker
3:00	COFFEE BREAK	
3:30	PROJECT REVIEWS	
	Fundamentals of Internal Strength Enhancement	R. Stratton

	On-line Measurement of Paper Mechanical Properties	G. Baum/C. Habeger
4:30	TOUR OF SELECTED PAPER MATERIALS DIVISION LABS	
5:30	SOCIAL TIME	
6:15	DINNER (CEC Dining Room)	
7:15	Fiber Strength in High Yields	T. McDonough

Wednesday, October 23

7:15 am	BREAKFAST (CEC Dining Room)	
8:00	DISCUSSION OF PROJECTS	Committee
10:00	COFFEE BREAK	
10:30	DISCUSSION OF PROJECTS (cont.)	Committee
11:15	CLOSING COMMENTS	
	Next meeting April 1-2, 1986	
11:30	ADJOURNMENT/LUNCH (CEC Dining Room)	

PAPER PROPERTIES AND USES
PROJECT ADVISORY COMMITTEE

Dr. Gary G. Homan (Chairman) -- 6/86*
Assistant Product Development Supt.
Westvaco Corporation
Wickliffe Mill
P.O. Box 278
Wickliffe, KY 42087
(502) 335-3131

Dr. H. Wayne Adickes -- 6/87
Vice President
Engineering and Development
Packaging Corporation of America
5401 Old Orchard Road
Skokie, IL 60077
(312) 470-2300

Dr. Alan F. Button -- 6/88
Director, Planning and Information Service
Champion International
West Nyack Road
West Nyack, NY 10994
(912) 578-7164

Dr. Barry W. Crouse -- 6/88
Director, Paper Technology Development
Eastman Kodak Company
Kodak Park
Rochester, NY 14650
(716) 722-0532

Dr. Hanuman P. Didwania -- 6/86
Principal Engineer
Container Corporation of America
Technical Center
450 East North Avenue
Carol Stream, IL 60188
(312) 260-3599

Dr. John L. Firkins -- 6/88
Director of Product Development
Thilmany Pulp and Paper Company
P.O. Box 600
Kaukauna, WI 54130
(414) 766-4611

Dr. Homan B. Kinsley, Jr. -- 6/86
Director of Technology, Filter Group
James River Corporation
P.O. Box 2218
Richmond, VA 23217
(804) 649-4219

Dr. Peter F. Lee -- 6/88
Director, Pulp and Paper Technology
Mead Corporation
Central Research
8th and Hickory St.
Chillicothe, OH 45601
(614) 772-3528

Mr. Christopher H. Matthews -- 6/86
Assistant Director of Paper Products
Union Camp Corporation
P.O. Box 3301
Princeton, NJ 08540
(609) 896-1200

Dr. Eugene C. Millard -- 6/88
Paper Mill Superintendent
Stone Container Corporation
Box 4068
Port Wentworth, GA 31407
(912) 964-1271

Dr. Vance Setterholm -- 6/86
Project Leader
USDA Forest Service
Forest Products Laboratory
P.O. Box 5130
Madison, WI 53705
(608) 264-5877

Dr. Gary Van Liew -- 6/87
Department Manager, Shipping
Container & Containerboard R&D
Weyerhaeuser Company
WTC 2h42
Tacoma, WA 98477
(206) 924-6464

*Date of retirement from committee.

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3469

COMPRESSIVE STRENGTH

October 22, 1985

PROJECT SUMMARY

PROJECT TITLE: COMPRESSIVE STRENGTH

PROJECT STAFF: W. J. Whitsitt/J. F. Waterhouse

PROGRAM GOAL:

Date: 9/10/85
Budget: $85,000
Period Ends: 6/30/86
Project No.: 3469

Identify critical parameters which describe converting and end-use performance and promote improvements in cost/performance ratios.

PROJECT OBJECTIVE:

To establish practical methods for enhancing compressive strength during paperboard manufacture.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

(1) The effects of cationic starch and cationic starch/PAE combinations on compressive strength and other properties have been investigated.

(2) The effects of inter and intra fiber polymer reinforcement using PVAc via solvent addition on compressive strength and other properties have been investigated.

(3) Further measurements have been made of the effects of handsheet forming conditions at high consistency on compressive strength and other properties.

(4) The effects of press type and drying restraint on sheet anisotropy and other properties have been investigated.

(5) The effect of certain commercial felt types on paper property development has been investigated.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

(1) Exploratory work has been done to determine the compressive strength potential of small wood coupons (16 mm x 16 mm) using ultrasonic characterization techniques.

(2) The effects of PAE, PAE/pearl corn starch additions on compressive strength and related properties has been determined.

(3) Formette linerboard handsheets have been made for investigating the effects of basis weight, fiber orientation and cationic starch addition on combined board strength and model evaluation (Project 3571).

(4) The surface addition of certain polymers to wet and dry Formette handsheets has been investigated. The polymers included pearl corn starch, cationic high M.W. starch and a polyvinyl acetate latex.

(5) The anisotropy of Formette handsheets dried under complete restraint is reduced by processes which improve bonding, e.g. refining, wet pressing, polymer addition, while the converse is true for processes which reduce bonding, e.g. calendering.

PROJECT TITLE: Compressive Strength

PROJECT STAFF: W. J. Whitsitt/J. F. Waterhouse

PRIMARY AREA OF INDUSTRY NEED: Properties related to end use

PROGRAM AREA: Improved converting processes and converted products

Date: 6/1/85
Budget: $85,000
Period Ends: 6/30/86
Project No.: 3469
Approved by VP-R:

PROGRAM GOAL:

Identify critical parameters which describe converting and end-use performance and promote improvements in cost/performance ratios.

PROJECT OBJECTIVE:

To establish practical methods for enhancing compressive strength during paperboard manufacture.

PROJECT RATIONALE:

Compressive strength is one of the most important end-use properties of linerboard, corrugating medium and other board grades. Because of this, ways to improve compressive strength are needed. Changes being implemented in Rule 41 provide impetus for research on compressive strength. In addition, however, future fiber and energy needs will encourage changes in board properties to place more emphasis on compressive strength. The research is expanding our knowledge of the compressive response of the board to papermaking processes and the relationships of compressive strength to elastic stiffnesses. These developments indicate there are ways to approach the objective through new papermaking strategies.

RESULTS TO DATE:

We have shown that compressive strength is highly related to the in-plane and out-of-plane elastic stiffnesses of paper. The relationship holds for commercial and experimental sheets made under a variety of conditions. This development suggests it will be possible to monitor compressive strength in the mill using ultrasonic techniques.

Compressive strength is enhanced by high densification, which increases bonding, and by high fiber compressive stiffness. Our results on oriented sheets indicate that compressive strength increases with refining, but even greater increases can be obtained by wet pressing to increase density. Within a practical range, higher CD compressive strength can be achieved by decreased fiber orientation and/or increased CD restraint during drying.

PLANNED ACTIVITY FOR THE PERIOD:

We will continue investigations of the compressive behavior of board as a function of composition, structure, and process variables. This includes effects of fiber properties, pulping, and papermaking variables; especially refining, wet

pressing, wet straining and drying. We will be using various types of high yield pulp made from both softwood and hardwoods. Exploratory work is planned to consider use of non cellulosic fibers and special strength additives. Practical methods for achieving suitable fiber-to-fiber bonding, sheet formation and directionality will be a necessary part of the work.

An important aspect of the work is how papermaking factors affect the elastic stiffnesses which govern the compressive strength as well as other properties. This will facilitate on-machine measurement applications.

STUDENT RELATED RESEARCH:

T. Bither, M.S.-1985; P. Ruthven, M.S.-1985

Status Report

COMPRESSIVE STRENGTH

Project 3469

We are continuing to explore opportunities for the improvement of compressive strength in the general area of raw material and papermaking process variables. The main thrust of our investigations during this period have been in the raw materials area.

RAW MATERIALS

Yield

In previous work we have briefly explored the area of ultra high-yield pulping, investigating both softwoods and hardwoods. Sulphonated mechanical pulps were made by the Chemical Sciences Division as part of their high-yield pulping development program. Although not yet a commercially feasible pulping process, this work did indicate that both high yield (~89%), sulphonated spruce, southern pine and red oak, each gave an equal or improved compressive strength performance when compared with our standard southern pine kraft pulp. The results of this work suggests that optimum compressive strength performance is not necessarily limited to a yield of 52% as suggested by some workers.

Determining the effect of pulp yield on compressive strength performance and related properties can be approached in a number of ways. There is the need to understand the limitations associated with increasing yield using current commercial pulping processes, i.e. kraft and NSSC; and also to determine in a more fundamental manner the influence the various cell wall components, i.e. lignin, hemicelluloses have on compressive strength. It is well known that strength related properties generally decline with increasing yield irrespective of the type of pulping process (commercial) employed. This is basically viewed as a bonding problem resulting from reduced fiber flexibility with increasing

yield. Approaches to improve interfiber bonding with increasing yield include press drying and sulphonation already mentioned above. It seems clear that if yield is to be further increased some form of chemical treatment will be necessary to offset the anticipated loss in performance potential, unless there are opportunities for blending pulps of different yield and refining level.

The compressive strength potential of the papermaking fiber is not only affected by yield but by possible "damage" to the fiber during pulping and fiber separation processes. An opportunity to determine both the effects of pulp yield and damage may be possible using ultrasonic characterization methods. It is proposed that small wood coupons be characterized at various stages of delignification using out-of-plane ultrasonic wave propagation methods. A preliminary investigation of this method employing 1.6 X 1.6 cm linerboard and wood coupons indicates that this approach is feasible for determining both the in-plane and out-of-plane elastic constants. Yiannos and Taylor* proposed a similar idea for making less tedious measurements of fiber elastic modulus.

Polymer Addition

The improvement of compressive strength performance via polymer addition is an attractive alternative, particularly in situations where improvements which can be made by refining, wet pressing and drying are limited. There are a number of chemical and physical factors to be considered in polymer addition, but we will be mainly concerned with the latter. A number of polymer systems, i.e. natural and synthetic are available. Obviously in practical applications we seek a cost effective system, however systems which are not cost effective or

*Yiannos, P. N., Taylor D. L. Dynamic Modulus of Thin Wood Sections. Tappi 50(1) January 1967. pg. 40-47.

commercially available may be employed for the purposes of clarifying mechanisms involved, e.g. the effects of intra fiber reinforcement on fiber compressive strength. Our selection of a particular polymer system is in part guided by the compressive strength model developed by Habeger and Whitsitt (we would also like to test its validity for boards with polymer addition) where the relative importance of in-plane and out-of-plane elastic constants has been demonstrated.

The in-plane and out-of-plane elastic constants should both be increased by improved interfiber bonding, and it will be important to determine how each is affected by selection of polymer type, location and method of addition.

In what follows we will report on our current work involving PAE, starch, and their method of addition.

PAE/Pearl Corn Starch

A series of handsheets having random fiber orientation were made on the Formette Dynamique using a southern pine unbleached kraft pulp having a 600 CSF. The nominal conditioned basis weight was 200 g/m^2. In one series PAE (Kymene 557H) was added at various levels up to 1.2%, and in another series following the same levels of PAE addition, 2.5% of an unmodified pearl corn starch was added. To determine if the order of addition was important, starch was added before the addition of PAE, at PAE addition levels of 0.2, 0.6 and 1.2%. The above polymers were added to the furnish in the Formette stock chest prior to formation and a mixing period of five minutes was allowed. The sheets after formation and couching were wet pressed and dried on the press-dryer combination using teflon spray treated blotters. An intermediate level of wet pressing load was chosen and held constant for this series of sheets. The results are given in Table 1 and graphed in Fig. 1-10. Figures 1-5 illustrate

Table 1. PAE, PAE/pearl corn starch, addition.

Starch/PAE	CSF	Apparent Density, g/m^3	$\bar{E}/\rho$, $(KM/sec)^2$	E_z/ρ, $(KM/sec)^2$	Comp. Strength σ_c/ρ, Nm/g	Tensile Strength σ/ρ, Nm/g	ε, %
0/0	621	0.612	7.54	0.219	25.3	49.2	3.09
0/0.2	669	0.634	8.18	0.234	28.5	58.3	3.54
0/0.4	688	0.633	8.08	0.246	30.5	66.4	3.91
0/0.6	723	0.632	8.15	0.244	31.7	67.9	3.85
0/0.8	733	0.633	8.16	0.239	31.8	69.3	3.96
0/1.0	755	0.629	8.07	0.237	31.4	71.0	3.94
0/1.2	732	0.638	8.17	0.246	31.3	74.4	3.99
PAE First							
0/2.5	622	0.630	7.60	0.202	25.4	51.3	3.10
0.2/2.5	653	0.627	8.03	0.228	29.3	61.9	3.63
0.4/2.5	684	0.632	8.04	0.229	29.9	66.6	4.02
0.6/2.5	701	0.639	8.06	0.238	31.3	71.1	3.99
0.8/2.5	704	0.631	8.23	0.244	32.9	70.4	4.01
1.0/2.5	717	0.634	7.98	0.240	31.5	74.5	4.18
1.2/2.5	710	0.642	8.02	0.255	30.5	74.0	4.17
Starch First							
2.5/0.2	637	0.632	7.98	0.230	29.2	62.7	3.75
2.5/0.6	707	0.637	8.21	0.256	31.0	71.7	4.08
2.5/1.2	717	0.638	8.15	0.241	31.9	74.4	4.10

changes in CSF, associated fines, and starch retention in the sheet with increasing PAE addition. The addition of PAE only, served to increase fines retention as evidenced by the increase in CSF shown in Fig. 1 and the reduction

in the weight of fines and color on the Formette backing blotter (situated below the forming wire) as shown in Figs. 2 and 3. A very good correlation was found between the amount of fines on the backing blotter and the color of the backing blotter. Using this relationship it was hoped to be able to differentiate between fines and starch loss in the presence of PAE. When starch is added, the increase in CSF is not as great as PAE alone, as shown in Fig. 1. We note from Figs. 2 and 3 that although the initial fines loss appears to be lower, it increases with increasing PAE in the presence of starch. It is interesting to note from Fig. 3 that the peak in fines loss at 0.8% PAE (and color, Fig. 2) occurs when starch retention is at a maximum, i.e. it appears that at this condition starch retention is preferential to fines retention. As shown in Fig. 5, PAE and PAE/starch addition contribute to sheet densification.

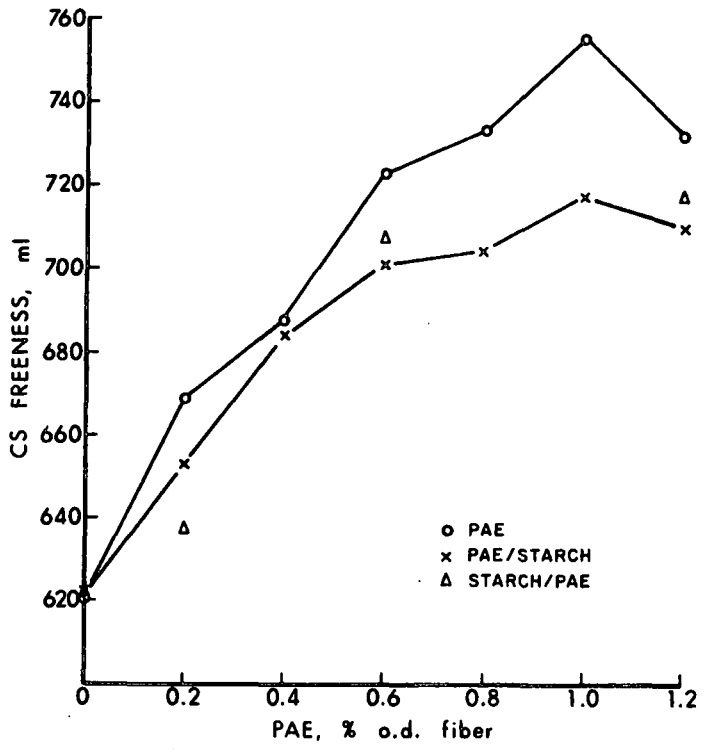


Figure 1. Variation of C.S. freeness with PAE and PAE/Starch addition.

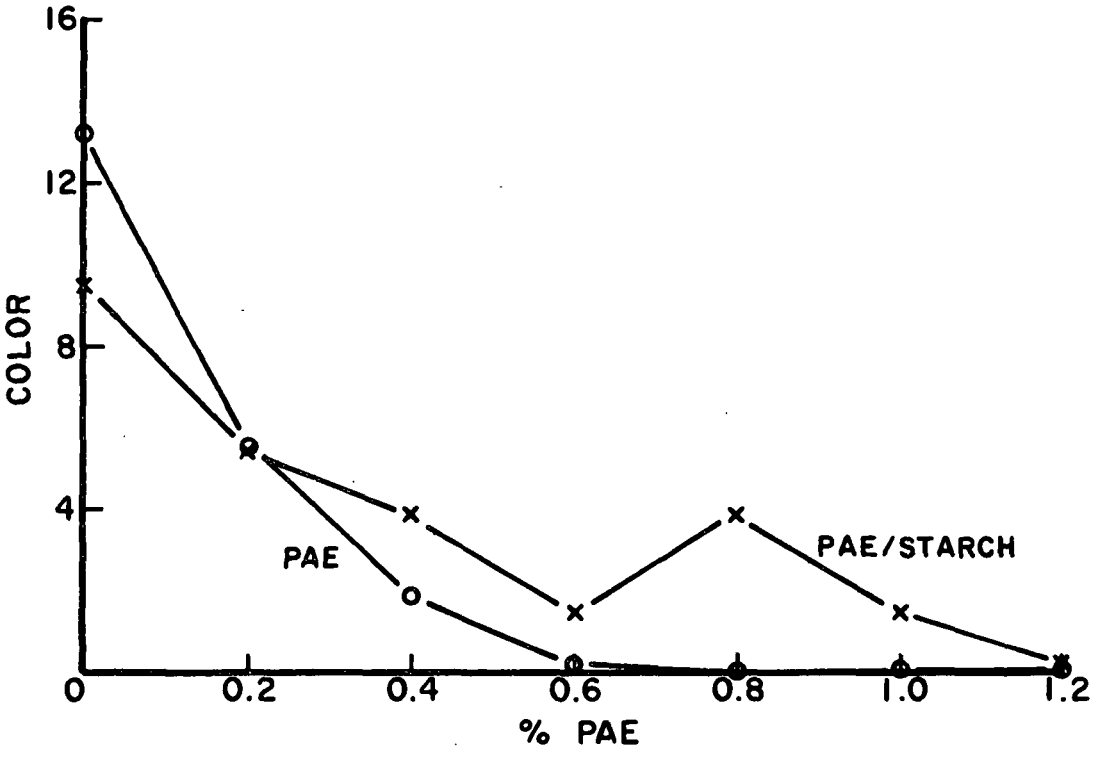


Figure 2. Color variation of Formette backing blotter with PAE and PAE/starch addition.

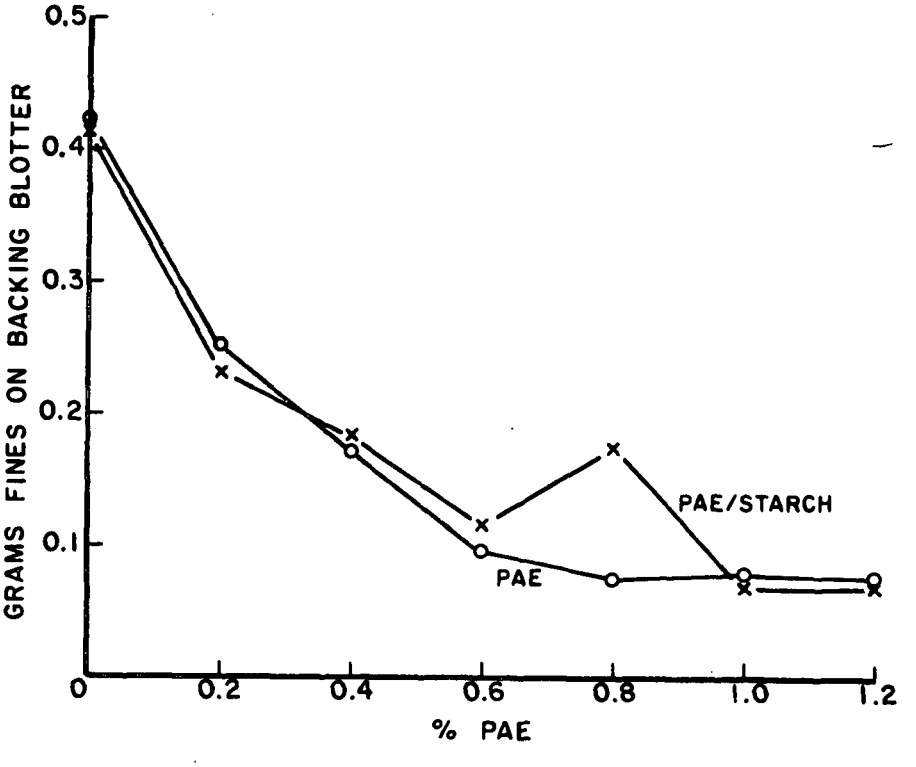


Figure 3. Effect of PAE and PAE/starch addition on fines loss.

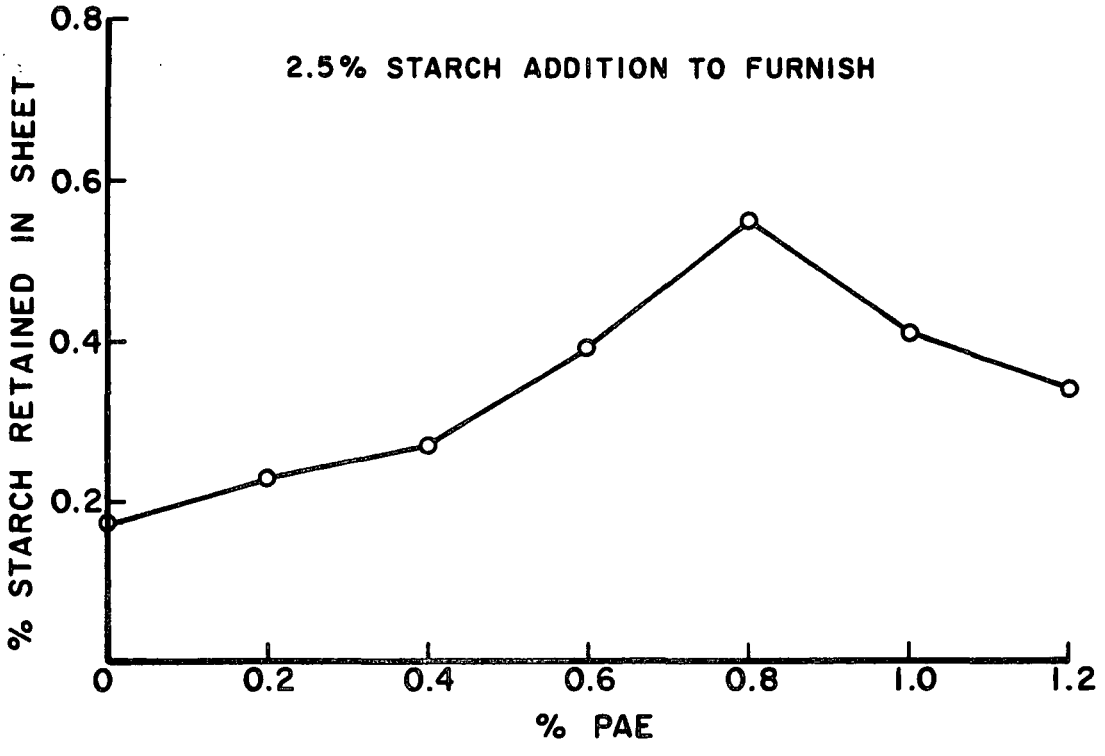


Figure 4. Effect of PAE on starch retention.

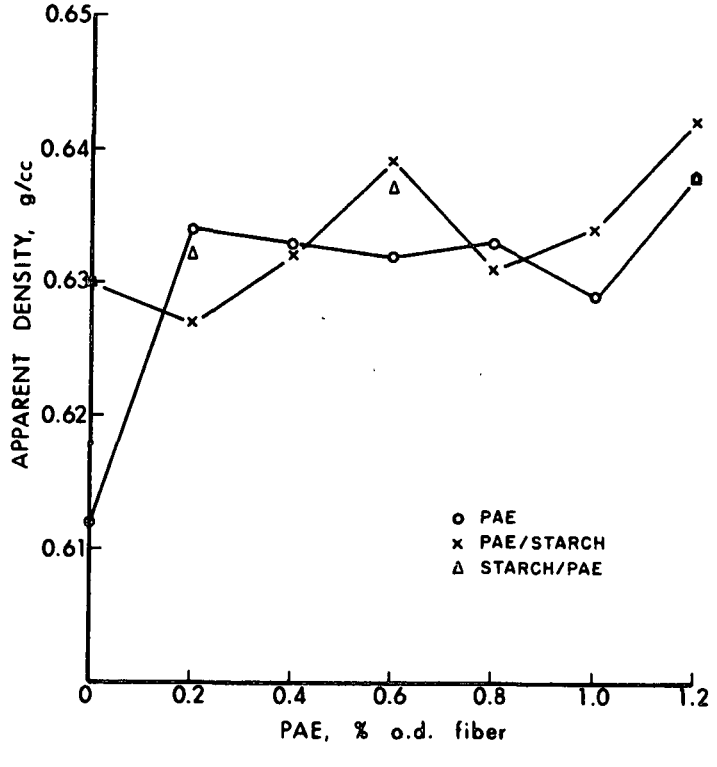


Figure 5. Variation of apparent density with PAE and PAE/starch.

Strength related improvements are shown in Figs. 6-10. The maximum improvement in compressive strength with PAE alone (see Fig. 6) is 26.5% at an addition level of 0.8%. When starch is used in combination with PAE an additional gain in compressive strength of 3.5% is found at the same level of PAE. The elastic properties shown in Figs. 7 & 8 tend to support the trends shown in compressive strength development, Fig. 6. Of particular interest is the differences in the variation of in-plane and out-of-plane properties with PAE, for the PAE alone and PAE/starch combination. Generally gains (or losses) in out-of-plane properties are partially offset by losses (or gains) in in-plane properties. Tensile strength and stretch performance are shown in Figs. 9 & 10. In this case the PAE/starch combination appears to offer a somewhat better performance than PAE alone at all PAE levels.

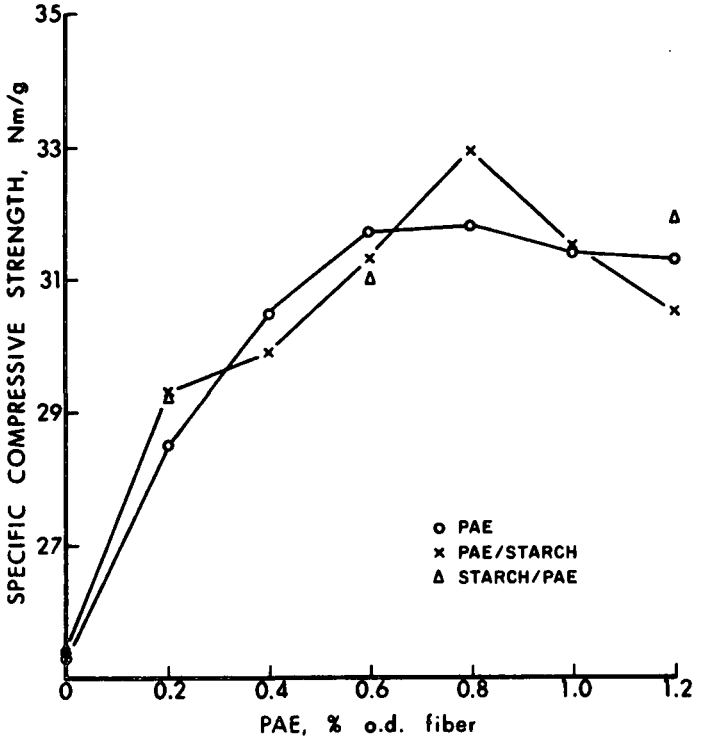


Figure 6. Variation of specific compressive strength with PAE and PAE/starch addition.

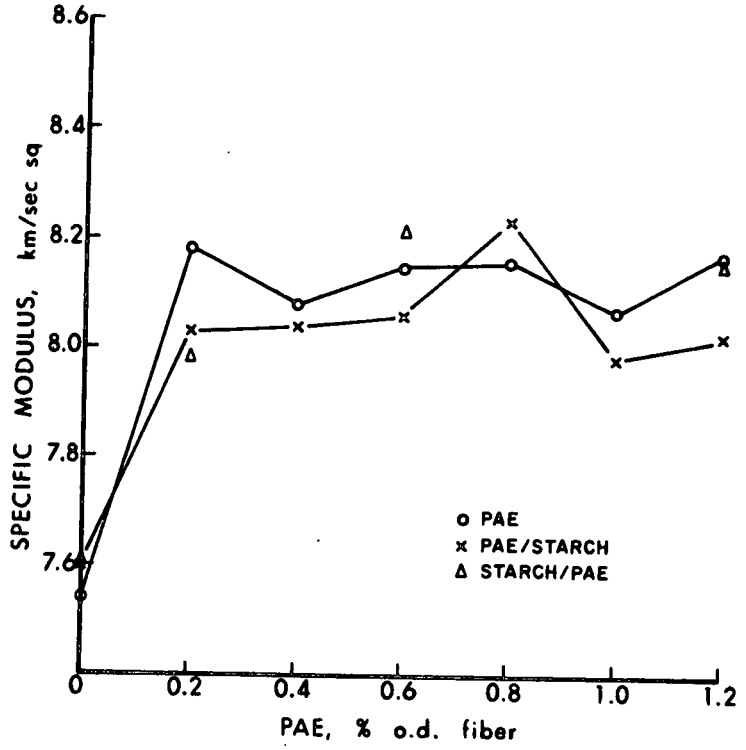


Figure 7. Variation of in-plane specific modulus with PAE and PAE/starch addition.

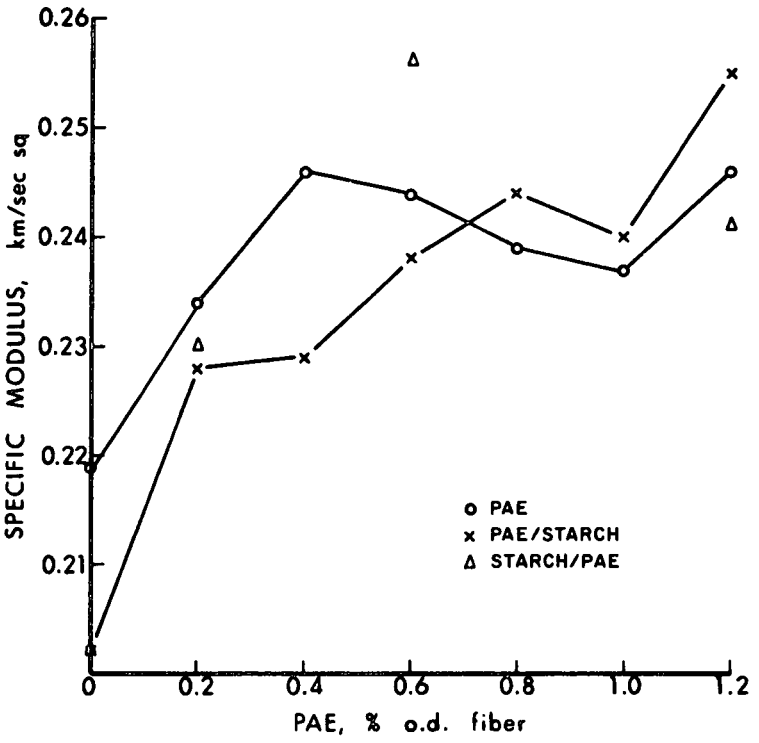


Figure 8. Variation of out-of-plane specific modulus with PAE and PAE/starch addition.

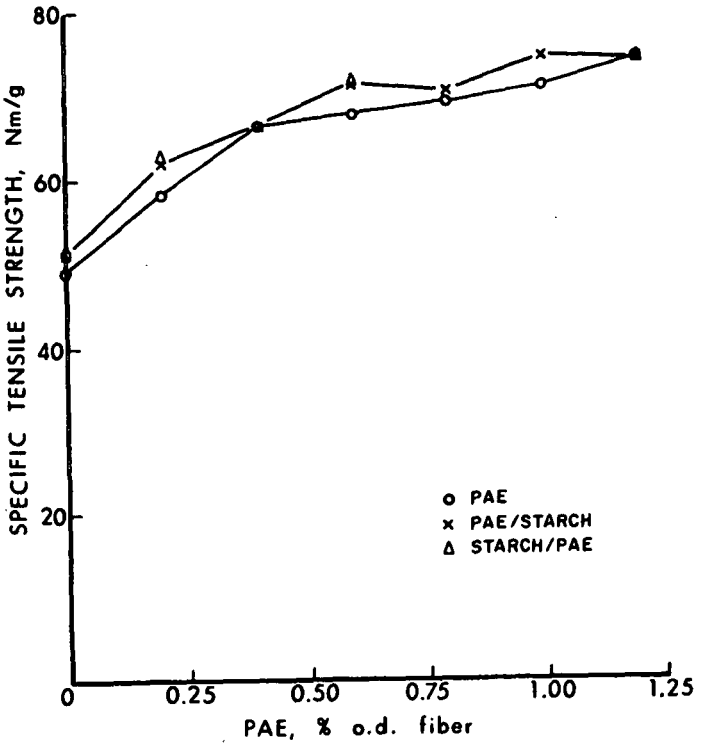


Figure 9. Variation of specific tensile strength with PAE and PAE/starch addition.

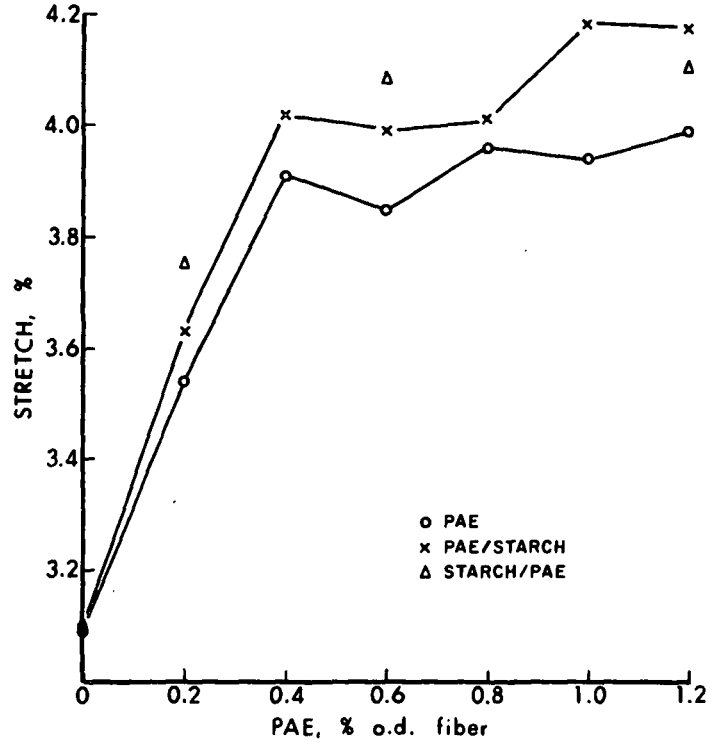


Figure 10. Variation of stretch with PAE and PAE/starch addition.

In summary, there are significant improvements in strength related properties with PAE addition to a whole pulp. The possibility of synergistic effects when using PAE in combination with an unmodified starch are also in evidence but we do not see the same level of improvement as found by Stratton and Becher in their work using a fines free pulp. Whether greater gains could be realized by treating a fractionated pulp with a PAE/starch combination and then adding back untreated fines is a possibility, albeit not a very practical one.

Recent unpublished work by Back of STFI indicates that compressive strength falls off much more rapidly than tensile strength with increasing moisture content, particularly in the range up to 10% moisture. Unfortunately we did not have sufficient samples left to measure both tensile and compressive strength variation with relative humidity and so only the compressive strength variation was measured and is shown in Figs. 11 and 12. It appears from Fig. 11 that there are no large differences in mean compressive strength loss between the treated and untreated board. In fact if we examine the percentage loss in mean compressive strength with increasing PAE more closely as shown in Fig. 12, we see an increase in compressive strength loss with increasing PAE addition at both 65% and 85% RH. It is also interesting to note, the small but consistent differences in compressive strength loss between the machine and cross machine directions of the sheet, i.e. the machine direction compressive strength losses are consistently lower than the cross machine losses.

Cationic Starch - Formette Dynamique

A series of linerboard handsheets have been made on the Formette Dynamique for Project 3571. The experimental design included the following variables: basis weight, fiber orientation, wet pressing load, and cationic high M.W.

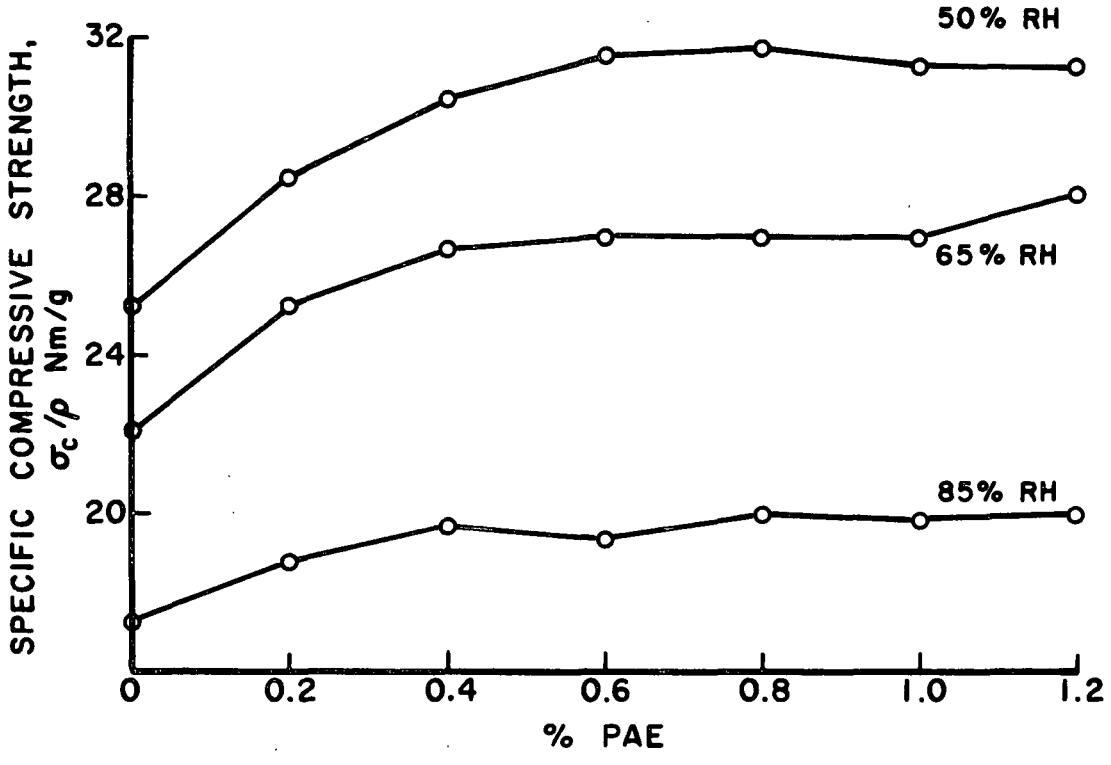


Figure 11. Variation of specific compressive strength with PAE addition at 50%, 65% and 85% relative humidity.

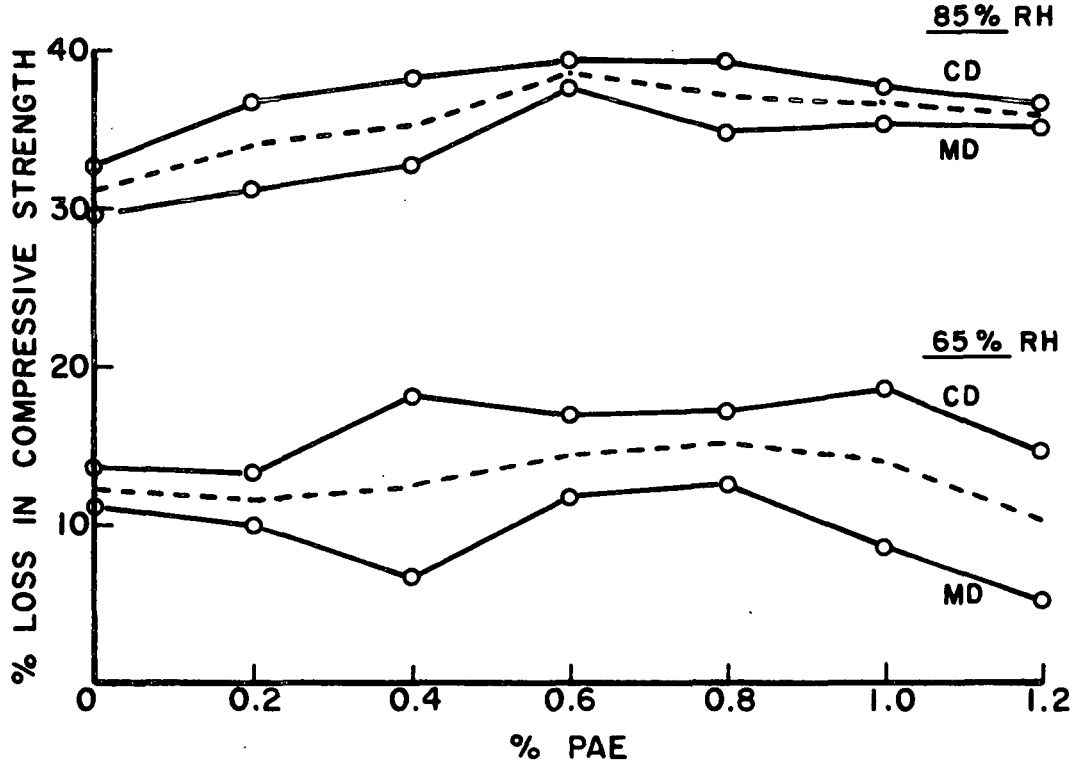


Figure 12. Percentage loss in compressive strength with PAE addition at 65% and 85% relative humidity.

starch addition. In earlier work we have reported compressive strength performance comparisons of cationic starch addition and wet pressing using the Noble and Woods handsheet former. Measurement and analysis of the Formette handsheet properties is not yet complete, however, preliminary data indicates that the compressive strength performance and cationic starch retention are comparable with that found in earlier work using the Noble and Woods former.

Method of Polymer Addition

There are three main methods of polymer addition: furnish, wet web and dry web. In addition, the choice of polymer location is a further consideration, i.e. intrafiber versus interfiber as well as its location in the thickness direction of the board. Our work to date has been mainly with furnish addition and in student related work we have attempted to investigate intra versus interfiber polymer reinforcement and hope that this work will continue. The exploratory work reported here is concerned with surface application of polymers to either the wet or dry web using spray and drawn down bar addition techniques.

The results shown in Table 2 are for the two sided spray application of an unmodified pearl corn starch to a Formette handsheet after couching. The two levels of starch addition are 2.5% and 5.0%. While the mean tensile strength and elongation show some improvement with starch addition the mean compressive strength shows virtually no change. However these same properties in the cross machine direction are significantly improved e.g. compressive strength is improved by 6.6% at the 2.5% starch addition level and by 13.2% at the 5.0% starch addition level. It is also noted that the anisotropy R as measured by the various property ratios decreases with starch addition.

Stained cross sections of the sheet, as seen under the light microscope, showed that the starch is deposited on the surface of the sheet with minimal

Table 2. Wet web spray addition of pearl corn starch.

Property	Control	Starch, % 2.5	Starch, % 5.0
Mean sp. mod. $\bar{E}/\rho$ $(KM/sec)^2$	6.92	6.79	6.77
R $(=E_{MD}/E_{CD})$	1.32	1.16	1.15
Mean sp. mod E_z/ρ $(KM/sec)^2$	0.129	0.127	0.125
Mean sp. comp. strength $\bar{\sigma}_c/\rho$ Nm/g	19.7	19.4	20.0
MD sp. comp. strength, Nm/g	22.0	20.2	20.2
CD sp. comp. strength, Nm/g	17.5	18.7	19.9
R (comp. strength)	1.25	1.08	1.01
Mean sp. tensile strength, Nm/g	38.8	40.7	42.8
MD sp. tensile strength, Nm/g	47.1	45.8	46.8
CD sp. tensile strength, Nm/g	31.9	36.2	39.1
R (tensile strength)	1.48	1.26	1.20
Mean tensile elong., %	2.3	2.64	2.61
MD tensile elong., %	2.26	2.48	2.55
CD tensile elong., %	2.30	2.81	2.67
Apparent density, g/cm^3	0.442	0.423	0.424

fiber penetration. This is consistent with the fact that there tended to be little penetration of the starch solution into the sheet during application. This made the sheet tacky and difficult to handle during subsequent drying. In fact, the sheets were dried between a teflon sheet and teflon spray treated blotters.

Drying the web without restraint (i.e. avoiding contact drying) to circumvent this problem is not desirable since it is anticipated that potential gains afforded by starch addition may be offset by losses due to unrestrained drying.

In a further series of experiments, the addition of a pearl corn starch, a low M.W. cationic starch, and a polyvinyl acetate latex by spray and draw down bar techniques were investigated. The strength properties are shown in Table 3 for the various polymer additions to the wet web after wet pressing, and to the dry web. Therefore sheets were dried sandwiched between a teflon sheet and an 84 X 86 mesh forming fabric with two blotters on the other side of the forming fabric. The tendency to stick was even greater with these sheets because of their higher apparent density and hence poorer starch penetration.

Table 3. Effect of polymer addition method on strength properties.

Sample	Polymer Content %	Basis Weight, g/m^2	A Density ρ_a, g/cm^3	E/ρ $(KM/sec)^2$	E_z/ρ $(KM/sec)^2$	σ/ρ, Nm/g	$\bar{\epsilon}$, %	σ_c/ρ, Nm/g
Control	0	194	0.787	7.89	0.263	48.5	3.54	27.5
Dry Web								
PVA_C	5.2	201	0.826	8.25	0.325	52.7	3.66	30.6
PVA_C	10.6	202	0.824	8.48	0.429	62.4	4.00	34.8
low mol. cationic starch	4.2	202	0.802	8.11	0.309	54.6	4.07	30.5
Pearl corn starch	2.0	202	0.775	8.05	0.267	49.6	3.88	26.9
Pearl corn starch	5.1	202	0.815	8.15	0.267	51.1	3.66	27.7
Wet Web								
Pearl corn* starch	4.1	200	0.698	7.93	0.177	51.0	2.93	27.0
Pearl corn starch	5.0	201	0.749	7.93	0.194	46.3	2.32	27.6
Pearl corn** starch	6.0	209	0.663	7.37	0.142	51.4	3.08	26.2

*2-sided application draw down bar
**2-sided application spray

The addition of pearl corn starch to either the wet or dry web did not result in an improvement in compressive strength, although there was, with one exception, a small improvement in tensile strength of about 5%. By contrast the low M.W. cationic starch and polyvinyl acetate latex both produced significant improvements in compressive strength and tensile properties. Nevertheless these gains are not as great (about 50% lower) as those found in earlier work with cationic starch using furnish addition.

PROCESS VARIABLES

Opportunities for the improvement of compressive strength in the area of papermaking process variables include:

1) refining
2) forming
3) wet pressing
4) drying

As stated earlier the main thrust of our work this period has been in the raw materials area. In previous work each of the above has been investigated with the main emphasis being on wet pressing and restraint during drying. Brief comments and a summary of our main findings in each of these areas are given below.

1) Refining: Refining improves compressive strength performance but it is likely to have an adverse effect on productivity and should therefore be kept to a minimum. No immediate programs are planned in this area although one possibility is to determine the effect of fiber curl and microcompressions on compressive strength.

2) Forming: Sheet formation does not appear to have such an adverse effect on compressive strength as it does on tensile strength, although it could still be an important factor in low basis weight mediums and liners.

3) Wet pressing: Densification by wet pressing is an important contribution to improving compressive strength, particularly if adequate steps can be taken to ensure the sheet is dried under full restraint. In student related work the effects of wet press felt type on strength related properties has been investigated. It was found that the felt type can influence property development, especially out-of-plane properties.

4) Drying: In previous work we have determined the importance of drying restraint on strength development using a press-dryer combination. Effective sheet restraint assumes greater importance as the level of wet pressing is increased.

In earlier work we have shown that the in-plane anisotropy of Formette sheets is, for a given fiber orientation, reduced by wet pressing. In other project work involving the Formette during this period, it appears that processes which increase bonding, e.g. starch addition, also tend to reduce anisotropy while processes which reduce bonding increase anisotropy, e.g. calendering, for sheets dried under full restraint.

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3571

BOARD PROPERTIES AND PERFORMANCE

October 22, 1985

PROJECT SUMMARY

Date:	9/10/85
Budget:	$150,000
Period Ends:	6/30/86
Project No:	3571

PROJECT TITLE: BOARD PROPERTIES AND PERFORMANCE

PROJECT STAFF: W. J. Whitsitt, R. A. Halcomb

PROGRAM GOAL:

Develop relationships between critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

- To develop relationships between container performance, combined board and component properties.
- To improve the performance/cost ratios of combined board (including medium).
- The short term goals are directed to (1) using structural ECT models to assess the impact of papermaking factors on board performance and (2) improving medium end-use performance properties.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS OF LAST PERIOD: (October 1984 - March 1985)

Section 1 - Corrugating Medium Improvement and Runnability.

(1) At a constant semichemical hardwood-to-softwood ratio of 75:25 oriented sheets were made as follows: (1) softwood in outside plies, (2) softwood in center ply and (3) blended control. The results indicated that at constant density.

   a. The highest STFI compressive strengths were obtained with the blend and the sheets with softwood outside.

   b. The ECT results of the three furnish constructions were about equivalent.

   c. The blended sheets tended to exhibit the highest flat crush strengths. The sheets with softwood in the inside ply gave somewhat lower flat crush strengths than the blend or the sheets with the softwood in the outer plies.

(2) Additional work on fiber-to-fiber bonding agents is in process.

(3) A part of the FKBG research program on corrugating medium is directed to determining what medium properties are required for high speed runnability, now and in the future. To supplement that research we are considering

models to relate critical corrugating speeds to medium properties and certain machine characteristics. As an initial step we are developing a model which relates flute fracture to (a) the frictional and tensile characteristics of the medium (2) nip geometry and (3) brake tension on the corrugator. A similar approach can be used to relate critical speeds for high-low flute formation to medium properties.

(4) The forces imposed in the medium during fluting depend importantly on the flute and roll geometry. Computer models of the nip geometry are being constructed so that the tensile and bending forces on the medium can be estimated and used in our modeling. Initial results indicate that:

a. The wrap angles which affect the tension in the medium vary cyclically during the formation of each flute. This gives rise to tension pulses during the formation of each flute.

b. Our analyses indicates that the medium draw or slippage is completed before the center of the labyrinth. Thus the tension forces reach their maximum before the center of the labyrinth. This is in accord with high speed motion pictures which show that fractures occur about a half-flute before the center.

c. Further analysis of flute and nip geometry should help clarify the effects of flute contour and roll geometry on high speed runnability.

Section 2 - ECT Results

(1) Modification of the FPL local buckling model to incorporate the elastic stiffnesses required empirical fitting of a number of constants, in some cases from limited data. Thus this approach proved to be complex and the results were not always in good agreement with experimental results.

(2) As an alternate a miniature plate model was formulated in two forms. One form utilizes STFI and flexural stiffnesses factors. The other form substituted elastic stiffnesses for the STFI along with the flexural stiffness factors.

a. In general the results indicated that ECT is primarily dependent on the STFI compressive strengths of the liners and medium. The influence of the flexural stiffness term was negligible.

b. In the second form the elastic stiffness terms for the compressive strength were also much more important than the flexural stiffness term. However, the prediction results were less satisfactory in some cases than obtained with the STFI compression results.

SUMMARY OF RESULTS THIS PERIOD: (March 1985 - September 1985)

Section 1 - Corrugating Medium Runnability and Improvement

(1) We have proposed a model which potentially relates critical corrugating speeds for high-lows, fracture and strength degradation to medium properties, nip geometry and operational factors.

(2) Our model indicates speeds which result in fracture will increase as the medium friction coefficient and thickness decrease, and tensile strength and stretch increase. These trends appear reasonable. Our initial comparisons of observed and predicted fracture speeds are encouraging.

(3) It appears that high-low flute formation should be related to the stress levels predicted from the model as a function of corrugator speed. The higher the stress level, the greater the high-lows. Thus it appears high-lows are influenced by the same medium properties listed above. However it may be necessary to take other medium properties into account.

(4) In addition to the medium properties the model indicates that fracture speeds will increase as the wrap angle and brake tension decrease and the flute tip radius increases.

(5) A computer program for analyzing flute profile and nip geometry effects has been developed. We are using this to provide input for our modeling and to consider better profiles for heavy weight mediums.

Section 2 - ECT Results

(1) To clarify the relative effects of linerboard compressive strength and flexural stiffness experimental linerboards have been made which have differing ratios of these properties. For this purpose we have varied density, directionality and an internal strength additive at three basis weight levels.

(2) Densification increased compressive strength but flexural stiffness decreased.

(3) Increasing MD/CD orientation decreased CD compressive strength but the geometric mean stiffness remained constant.

(4) A starch additive was also used. It slightly increased both compressive strength and flexural stiffness.

(5) These changes in papermaking factors affected the desired variations in linerboard strength/flexural stiffness ratios. We have combined the linerboards with a 26-lb medium and are proceeding to evaluate their ECT strengths.

PROJECT TITLE: Board Properties and Performance

PROJECT STAFF: W. J. Whitsitt, R. A. Halcomb

PRIMARY AREA OF INDUSTRY NEED: Properties related to end uses.

PROGRAM AREA: Performance and Properties of Paper and Board.

Date: 6/1/85
Budget: $150,000
Period Ends: 6/30/86
Project No: 3571
Approved by VP-R:

PROGRAM GOAL:

Develop relationships between critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

- To develop relationships between container performance, combined board and component properties.
- To improve the performance/cost ratios of combined board (including medium).
- The short term goals are directed to (1) using structural ECT models to assess the impact of papermaking factors on board performance and (2) improving medium end-use performance properties.

PROJECT RATIONALE:

There are many aspects of box and combined board performance which have not been adequately related to board properties through structurally sound models. Such structural models identify the critical board properties needed for end-use performance. They can then be used to select papermaking approaches to maintain or improve box performance at less cost. An important step is to incorporate the elastic stiffnesses of the board into such models is possible. This will allow us to use our developing knowledge on how papermaking factors affect the elastic stiffnesses to make board improvements.

RESULTS TO DATE:

Rayleigh-Ritz methods have been used to analyze container failure under several types of load. Finite element techniques have been used to model the bending behavior of container board. Analysis of present ECT vs. component local buckling models indicates they fail to predict ECT performance when the liner or medium density is changed. In the case of medium we have shown that the compressive strength is lowered by high bending and shear stresses imposed during forming. These losses in strength lower flat crush and ECT. The losses are inversely related to the density and Z-direction elastic stiffness of the medium. Densification via wet pressing is one way to improve end-use performance of medium.

PLANNED ACTIVITY FOR THE PERIOD:

The relationships being developed will show how the elastic stiffnesses and compressive strengths of the components will affect combined board ECT. The analysis will help us assess the relative importance of compressive strength and the bending stiffnesses of both the liners and medium in determining ECT performance. We will need to confirm and validate the relationships using components made under various papermaking conditions as well as commercial boards.

Our research on medium shows that densification via wet pressing improves strength retention during fluting and gives higher ECT and flat crush in the combined board. We will continue this research and extend it to consider other ways to improve formability and performance. This will include work on sheet structure, the use of additives and pressing variables.

As an outgrowth of this and related work for FKBG we will investigate ways to show what properties of the linerboard and medium are required for high-speed runnability on the corrugator. Runnability refers to the critical speeds associated with strength retention, the development of high-lows and flute fracture.

POTENTIAL FUTURE ACTIVITIES:

Application of similar techniques to end-use failures involving flexure, shear and combined tension, flexure and shear.

Status Report

BOARD PROPERTIES AND PERFORMANCE

Project 3571

INTRODUCTION

The objectives of this program are to (1) develop relationships between container performance, combined board and component properties and (2) determine ways to improve the cost/performance ratios of linerboard and medium. To fulfill these objectives we must consider the end-use and processing requirements. This requires consideration of medium and liner properties, operational conditions in the corrugator and flute geometry. At the same time our objective is to find ways to maintain or improve combined board and box performance while maintaining runnability. For these reasons our current work is divided into two parts, namely (1) process research and (2) ECT/box compression performance.

PROCESS RESEARCH

The current trend is to use higher corrugating speeds and we can expect higher target speeds in the future. Higher speeds place increasing demands in the forming characteristics of the medium and the bonding process. Concurrently there are papermaking changes underway which will affect the runnability and end-use properties of board. To use our board materials effectively as speeds increase we need to improve our understanding of what properties are needed for high speed runnability. Parts of the current FKBG research program are directed to this objective.

To supplement the FKBG research we are developing models which will explain how critical corrugating speeds are dependent on medium properties and corrugator operational factors. The models are based on physical analysis of the corrugating process but are partly empirical at this time.

Our approach to modeling flute fracture and high-lows is briefly discussed below. At this stage the speeds shown on the graphs should be regarded as relative values. Work is in process to determine what adjustments are needed.

Applied Stresses and Flute Fracture

We hypothesize that flute fracture occurs when the induced stresses due to bending, friction and dynamic effects exceed the tensile strength of the medium. (Note: the model can be written in terms of either stress or strain.) The following equation is proposed:

$$(T_o + S_f/k_1)e^{\mu\theta} + k_2T_b = T_f \qquad (1)$$

where T_o = brake tension

S_f = fracture speed

θ = total wrap angle in labyrinth to cessation of slippage

μ = coefficient of friction

T_b = tension in outer layer induced by bending

T_f = tensile strength of medium

k_1 = empirical constant

k_2 = empirical constant

At present the bending strain T_b is being estimated as follows.

$$T_b = 50\ T_f t/[\varepsilon(r + t/2)] \qquad (2)$$

where T_f = tensile strength of medium

t = thickness of medium

ε = medium stretch, %

R = radius of curvature of flute tip

Equation 1 gives the following relationship for the fracture speed S_f:

$$S_f = (k_1/e^{\mu\theta})[T_f - k_2T_b - T_oe^{\mu\theta}]$$

Note that for a given medium and nip geometry, speed is a linear function of the brake tension T_0. This is in accord with past data (Fig. 1) and has been confirmed in current work for FKBG.

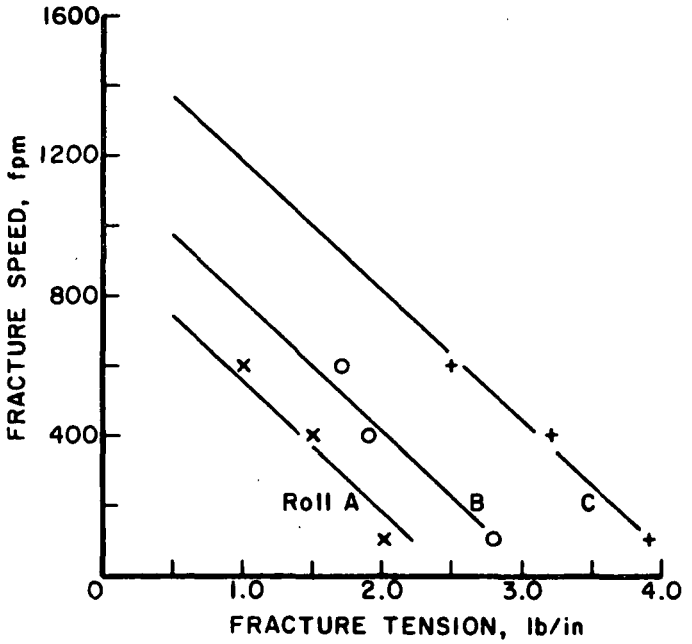


Figure 1. Fracture speeds (S) are approximately linearly related to brake tension (T), i.e. S kT.

For comparative purposes past Institute data from several sources were used to estimate values for the empirical constants. Taking a wrap angle of 4.09 radians, gave the following estimates: $k_1 = 370$; $k_2 = 0.075$.

Using these constants Figs. 2-4 show the effects of the medium properties on projected speeds to flute fracture. In Fig. 2 fracture speed increases with increasing tensile strength and decreasing coefficient of friction. Figure 3 shows that increasing stretch increases the fracture speed. Figure 4 indicates that decreasing medium thickness increases the projected fracture speed. These projected trends seem reasonable based on past experience but the magnitude of the effects must be verified.

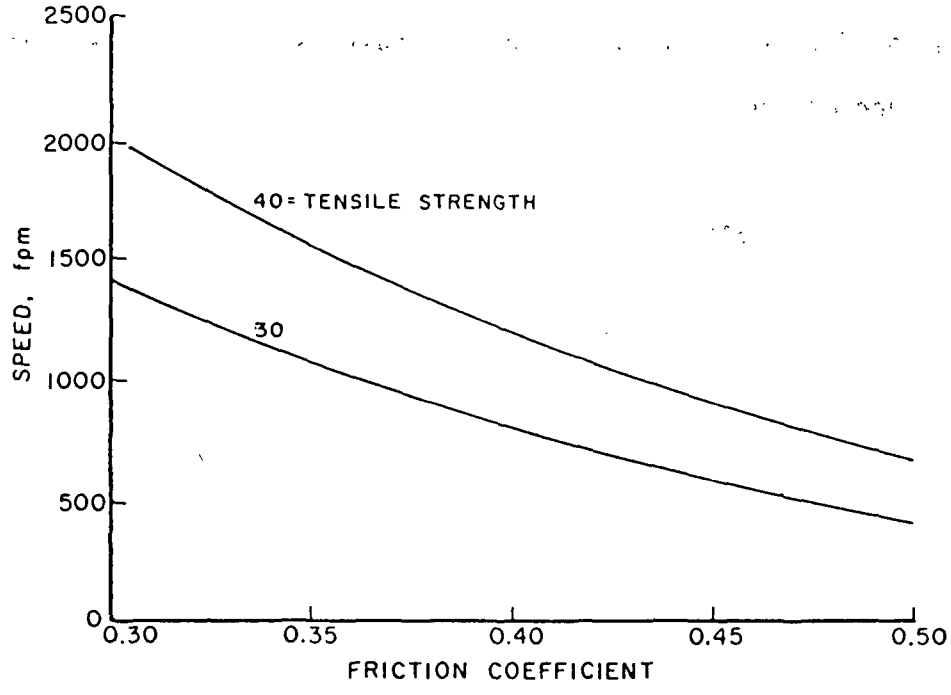


Figure 2. Speed vs. friction coefficient and tensile strength (other factors held constant).

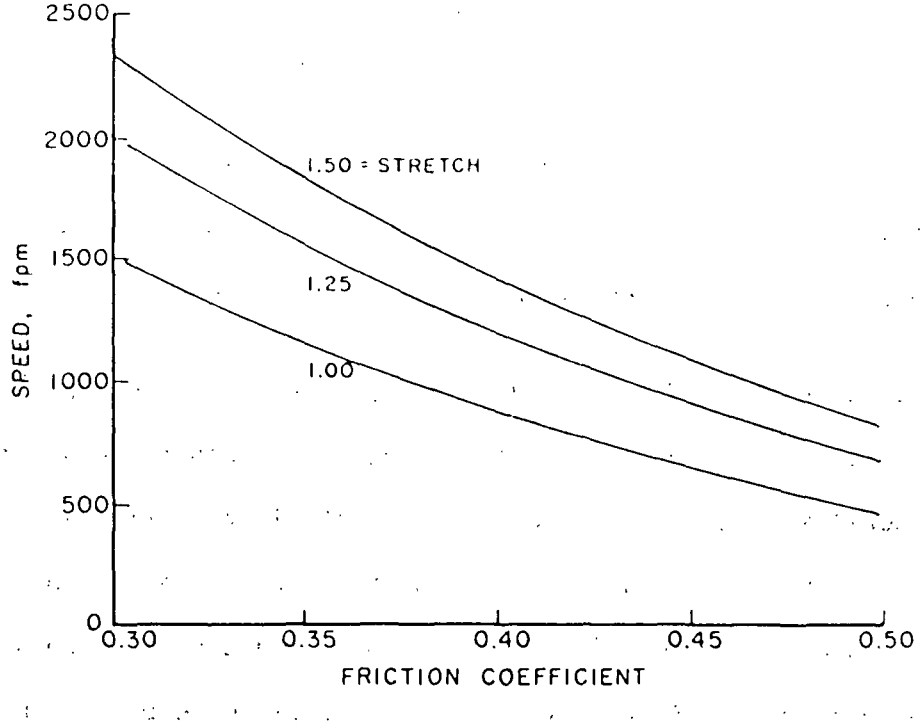


Figure 3. Speed vs. friction coefficient and stretch (other factors held constant).

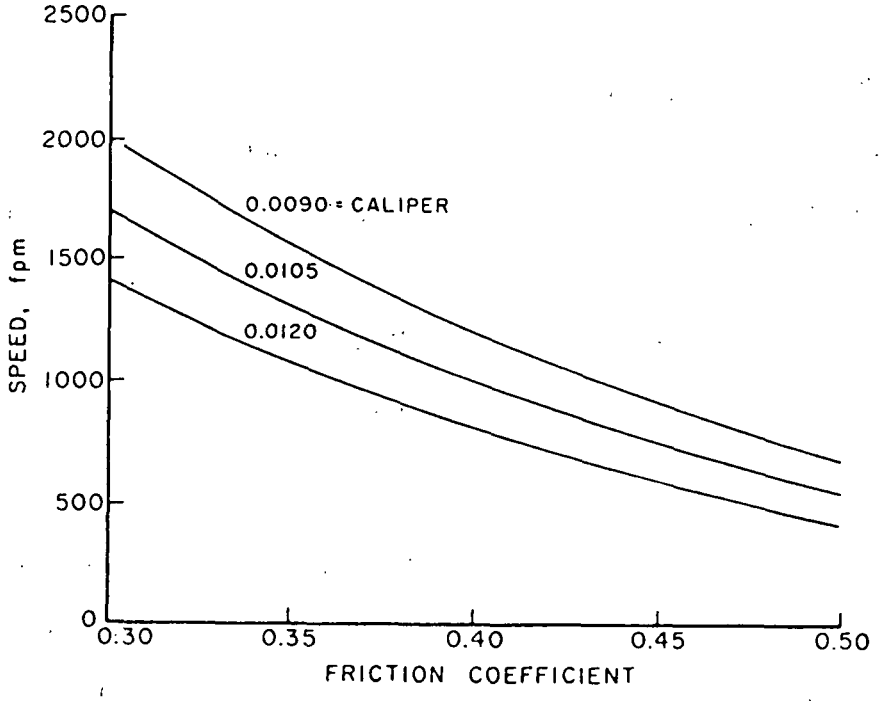


Figure 4. Speed vs. friction coefficient and medium thickness (other factors held constant).

Our current high speed runnability trials for FKBG are providing an opportunity to further develop and check the model concepts. Preliminary results on several 26-lb mediums have allowed us to re-estimate the constants in Eq. 1 as follows: θ = 3.09 radians, k_1 = 297 and k_2 = 0.0979. These are not greatly different from our original estimates so the trends shown in Figs. 2-4 are valid. With these constants, we obtain fairly good agreement between observed and estimated fracture speed for these 26-lb mediums. Also where the projected speeds are above our maximum corrugating speed of 1000 fpm, we generally can run such mediums at 1000 fpm without visible fracture. We believe these results are encouraging. As additional runnability data is obtained we will refine our estimates of the constants and check the effects of the various medium properties and other factors.

In addition to the medium properties the model indicates that fracture speeds will increase as the wrap angle and brake tension decrease and the flute tip radius increases. These effects also appear to be physically reasonable.

In-plane stress intensity

If S is given some value less than the fracture speed, then the left side of Eq. 1 is an estimate of the total applied tensile stresses at that speed. As speed is increased the total stress increases. Fracture occurs when the applied stress exceeds the tension stress. Dividing the applied stress at a given speed by the tensile strength provides an estimate of the applied stress intensity ratio at the given speed.

For example, Fig. 5 shows that the stress intensity ratio increases linearly with increasing speed. For a given stress ratio the medium with the lower friction coefficient will tolerate higher speeds. Conversely for a given speed the medium with the lower friction coefficient will be stressed less severely.

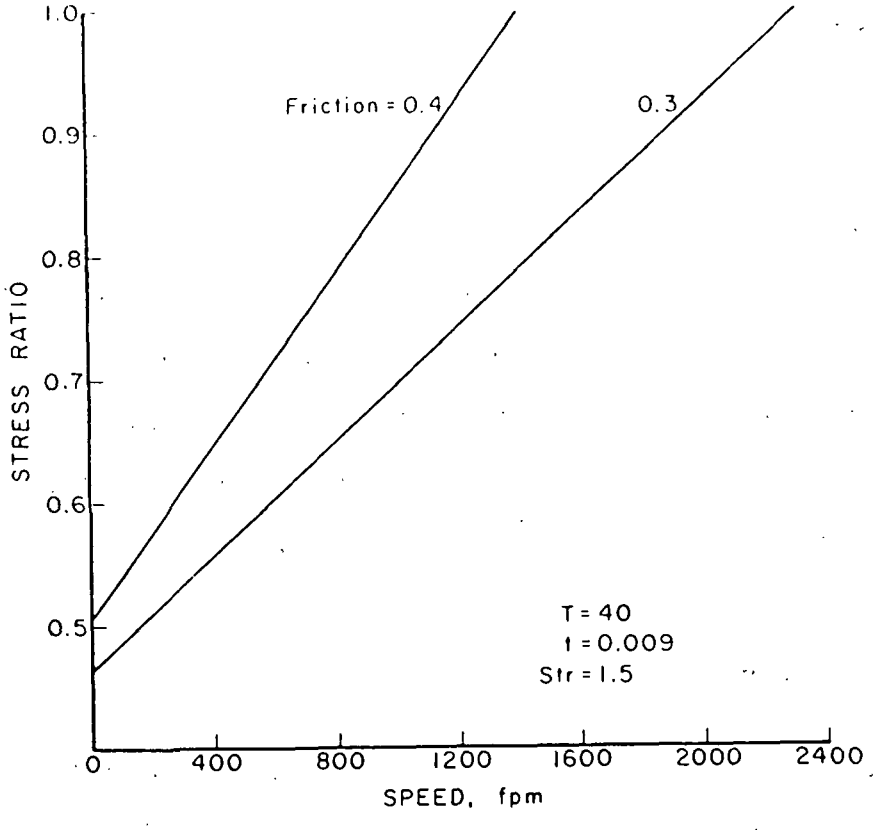


Figure 5. Applied stress intensity ratios increase with speed to the fracture level at a ratio of unity.

Similar graphs are obtained for the other medium properties. At a given speed lower stress intensities are obtained with higher tensile strengths, stretch and lower thickness. Higher brake tensions give rise to higher stress intensities at a given speed as would be expected.

High-Lows

High-lows are a manifestation of form instability, i.e. the medium attempts to relax back to a flat shape but in a non-uniform way. A portion of the strain applied during forming will be non-recoverable, the remaining portion will be recoverable and contribute to form changes. In general, both components should increase as the applied stress increases. This would explain why high-lows become more pronounced as speed increases. Also as the stresses increase toward fracture, local variations in stress and strain which are associated with paper machine formation should become more pronounced. These local variations in strain would manifest themselves as differences in recoverable and non-recoverable stretch (or TEA) in localized regions. Thus paper machine formation can influence high-lows through its effects on the variability of medium properties.

Thus, there is reason to believe that high-low flute formation should depend on the applied stress intensity. The latter will depend on the material and process factors associated with the model.

For example, Fig. 6 shows that the high-lows obtained at several speeds for three mediums are well related to calculated stress-ratios. High stress ratios promote high-low flute formation.

Their findings are encouraging. Even at this stage they are providing a physically reasonable basis for identifying the medium properties which are

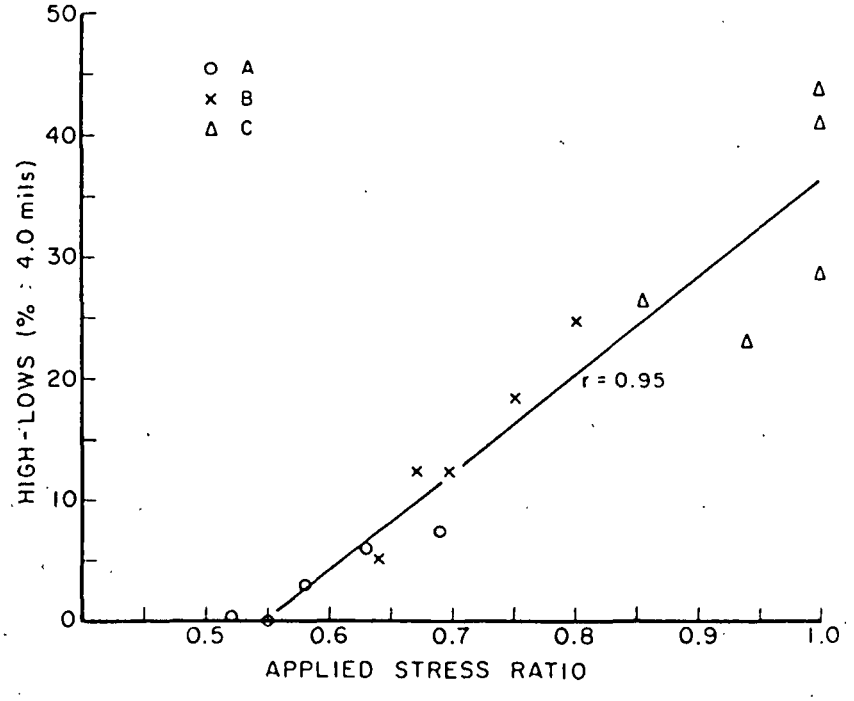


Figure 6. High-lows are linearly related to the applied stress ratios.

required for high-speed forming. Probably it will be desirable to expand the model to include other factors such as medium compressibility, strain rate, and moisture, and temperature effects as we develop more theoretical and experimental information.

Nip and Flute Geometry

To support our research in fluting we have developed means for analyzing nip geometry and flute profile effects on draw factor, wrap angles, flank and tip clearances and other factors related to corrugating performance. Potentially it should be possible to estimate the tension and bending stresses imposed on the medium during corrugating.

From contour measurements on corrugating roll castings our calculations indicate that the medium draw or slippage is completed before the center of the

nip (Fig. 7). This helps define the total active wrap angle in the labyrinth, and hence the tension forces due to friction. The total wrap angle will depend on the flute contour and roll diameter.

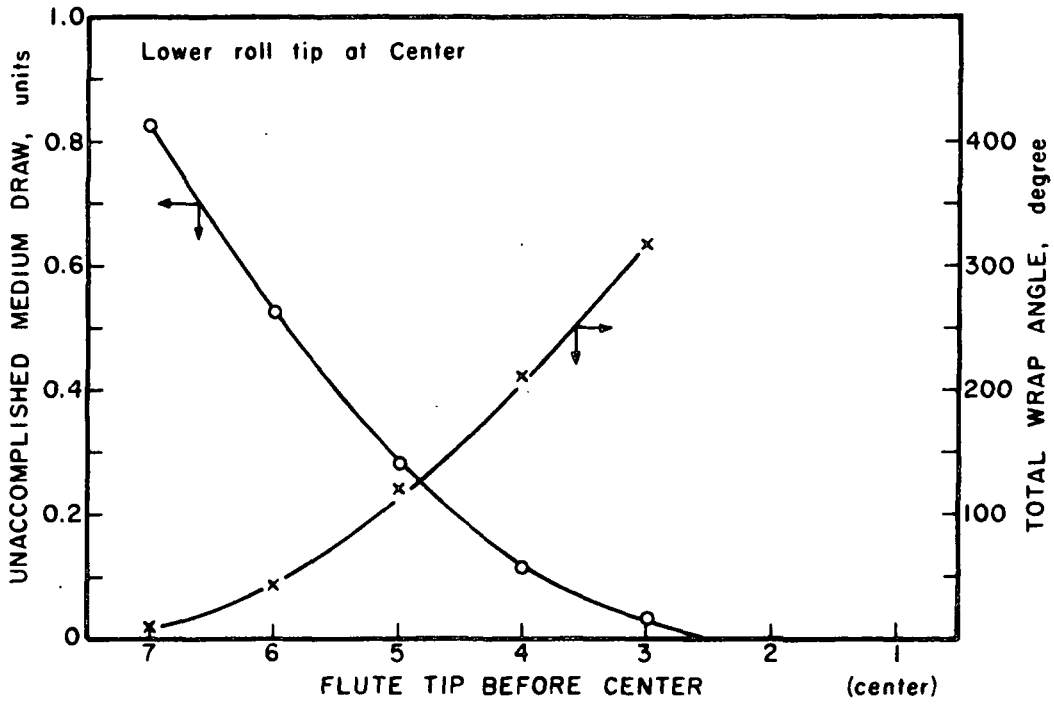


Figure 7. Unaccomplished medium draw and total wrap angle as a function of flute tip position in labyrinth.

The wrap angles which affect the tension in the medium vary cyclically during the formation of each flute as mentioned in the previous report (Fig. 8). This gives rise to tension pulses during the formation of each flute. Web tension measurements on the corrugator confirm this effect; relatively large cyclical fluctuations about the average tension are always obtained. More information is needed on how these fluctuations are affected by medium friction, speed and other operating conditions.

One portion of our FKBG research is concerned with improving the corrugating performance of heavy weight corrugating mediums. More fluting damage

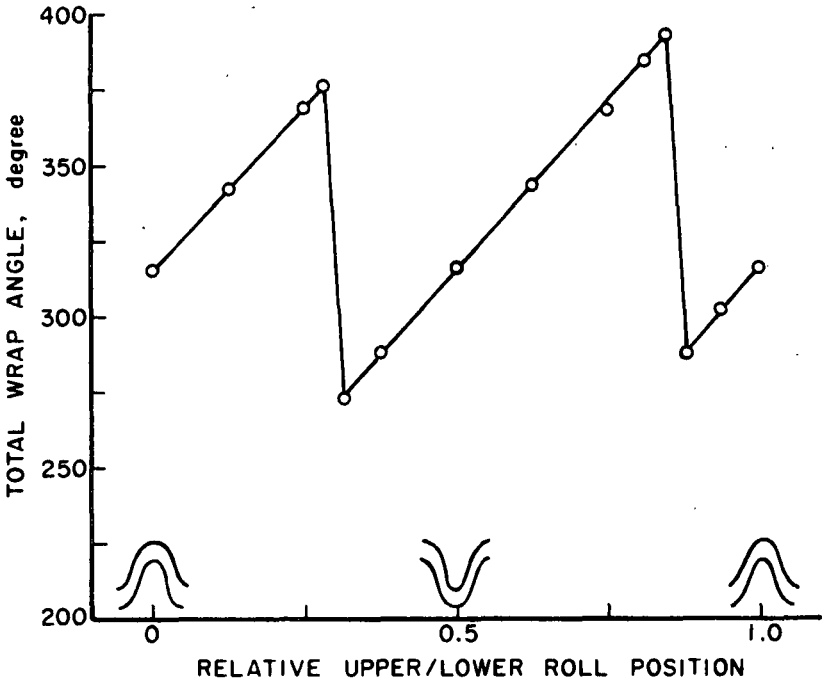


Figure 8. Total wrap angle varies cyclically during formation of one flute, thus tension on medium will also vary.

occurs in the case of heavy-weight, thick mediums because flute profiles are designed for 9 point medium. Typically, profiles are designed so that the flank clearance is 9 mils when the tip clearance is about 6 mils. Thus minimal pressure is exerted on the flanks for 9 mil medium. However this is not the case for thick, heavy-weight mediums. Computer analyses of roll geometry show that the flank regions of the flute will be compressed to a greater degree as the medium thickness is increased. This has been confirmed by local caliper measurements on fluted mediums of various thicknesses. Various profiles shapes to improve fluting of heavy-weight mediums are under study.

Strength Retention -- Improvements on Medium Properties

Parts of our past work have been directed to making improvements in medium properties to prevent strength losses during fluting and, hence, improve performance. The medium loses about 40% of its MD and 20% of its CD compressive

strength potentials during fluting. These losses occur due to the high bending strains imposed on the medium during fluting and are aggravated by high web tensions in the forming nip. By reducing these losses in strength we could achieve savings in the manufacture of medium.

Our past work shows that densification of the medium via wet pressing is an effective way to reduce forming losses. Such mediums exhibit higher flat crush strengths and ECT when made into corrugated board. We have also shown that such mediums can be bonded satisfactorily in the single-facer even though they are less porous. It is possible that some adhesive formulation adjustment might be required depending on the degree of medium densification.

While we have carried out limited studies of other papermaking factors, we are currently considering the use of additives to improve fiber bonding of mediums. Linerboard trials with starch are discussed in a later section of this report. Other work in additives is being carried out under Project 3469. That work should help determine where the additive should be located for best results, -- i.e. on the surfaces or distributed through the sheet. In addition we are planning new work on directionality effects, paper machine formation and dry calendering.

ECT RESEARCH

It has been found in earlier studies that a dominant factor in determining box compressive strength performance is the short column strength (ECT). The goal of this project is to find a model which will adequately predict ECT from the properties of the individual components. In particular we are investigating models into which we can incorporate the elastic stiffnesses. This would enable us to use our developing knowledge on how papermaking factors affect the elastic

stiffnesses to assess their impact on ECT strength. We have focused our recent attention primarily on two models: the Forest Products Laboratory (FPL) local buckling model and a model which utilizes the approach taken by the Institute in developing the McKee top load box compression formula.

The FPL Model

The FPL model was developed in the late 1970's by M. W. Johnson, Jr., T. J. Urbanik and W. E. Denniston. It consists of a theoretical structural analysis of combined board and a computer algorithm for solving the equations. The model predicts compressive strength values for balanced single wall combined board based upon information about the flute geometry and the individual components. The model assumes that the components are isotropic and that their stress-strain curves can be described by hyperbolic tangent formulas. The FPL model's predictions for ECT are sensitive to the individual component stress-strain curves and the curves, in turn, are dependent upon the particular type of compression test apparatus with which they are obtained.

Past Institute work has shown the FPL models predictions based upon the FPL vacuum uniaxial compression tester to be superior to the FPL model's predictions based upon a Weyerhaeuser lateral support device.

Several attempts were also made at the Institute to adapt the FPL model to incorporate either STFI values or elastic stiffnesses in place of stress-strain curves. While these attempts achieved moderate success, they required the introduction of several empirically determined fitting constants.

Flexural Stiffness Model

Another approach to analyzing combined board ECT is to approach the problem in the same way as the Institute top load box compression formula. Following

this approach the liner contribution to ECT is formulated at the product of two terms:

$$\left[\begin{array}{l}\text{Compressive strength}\\ \text{of the linerboard}\end{array}\right]^{b} \cdot \left[\begin{array}{l}\text{Geometric mean flexural}\\ \text{stiffness of liner}\end{array}\right]^{1-b}$$

and the medium's contribution is formulated similarly as

$$\left[\begin{array}{l}\text{Compressive strength}\\ \text{of the medium}\end{array}\right]^{c} \cdot \left[\begin{array}{l}\text{Geometric mean flexural}\\ \text{of medium}\end{array}\right]^{1-c}$$

where b and c are constants to be experimentally determined. The combined board ECT prediction is then the sum, with the appropriate multiplicative factors, of these two expressions plus an additive constant. This approach was investigated in two forms: (1) using STFI as the measure of the component's compressive strength and (2) using $(E_y t)^{0.75}$ $(E_z t)^{0.25}$ as the measure of the component's compressive strength. In both forms the flexural stiffnesses were estimated from elastic stiffness measurements. When the STFI values were used with a set of 85 commercial boards made from various component grades, the constants b and c were approximately equal to 1.0. Thus the flexural stiffness terms seemed to have no effect on ECT. The average predictive accuracy of the 85 boards was about 3.7%. When this STFI form was applied to a set of 23 experimental boards using the regression constants determined from the set of 85 commercial boards, the average predictive accuracy was 6.9%.

In the alternative form using $(E_y t)^{0.75}$ $(E_z t)^{0.25}$ in place of STFI as the measure of component compressive strength, the empirically determined values for b and c for the set of 85 commercial boards were 0.87 and 1.0, respectively. These values indicated that the flexural stiffness term for the liner had a

small effect on ECT while the medium's flexural stiffness had no effect. The average predictive accuracy for the 85 commercial boards was about 3.6%

Experimental Validation Tests

The above results based on 85 commercial boards indicated that the compressive strength terms were much more important than the flexural stiffness terms. The present experimental study was undertaken in an attempt to validate this result using combined boards made from components with varying ratios of compressive strength to flexural stiffness.

For this purpose linerboards with varying densities and directionalities at three basis weight levels were made according to the experimental design shown in Table 1. For each of the three basis weights and each of the three density levels linerboards were made at a target directionality of 2:1. At the medium density, linerboards were made having target directionalities of 3:1, 2:1 and 1:1. (Note: actual MD/CD stiffness ratios were about 3, 2.5 and 1.)

Table 1. Experimental sheet variations.

Basis Weight	Low Density	Medium Density	High Density
33 lb	D = 2:1	D = 3:1, 2:1, 1:1	D = 2:1
42 lb	D = 2:1	D = 3:1, 2:1, 1:1	D = 2:1
69 lb	D = 2:1	D = 3:1, 2:1, 1:1	D = 2:1

D = directionality target; actual MD/CD stiffness ratios were about 3, 2.5 and 1.

Figure 9 shows densification increased the CD STFI when the MD/CD directionality was held constant at about 2.5. This result was in agreement with previous work of this nature done at the Institute. Figure 10 shows a similar

increase in our compressive model expression $E_y t^{0.75} E_z t^{0.25}$ as density increased. This would be expected. The decrease in CD STFI with increase in directionality at about equal density is shown in Fig. 11. Figure 12 shows a similar decrease in $E_y t^{0.75} E_z t^{0.25}$ with increasing directionality.

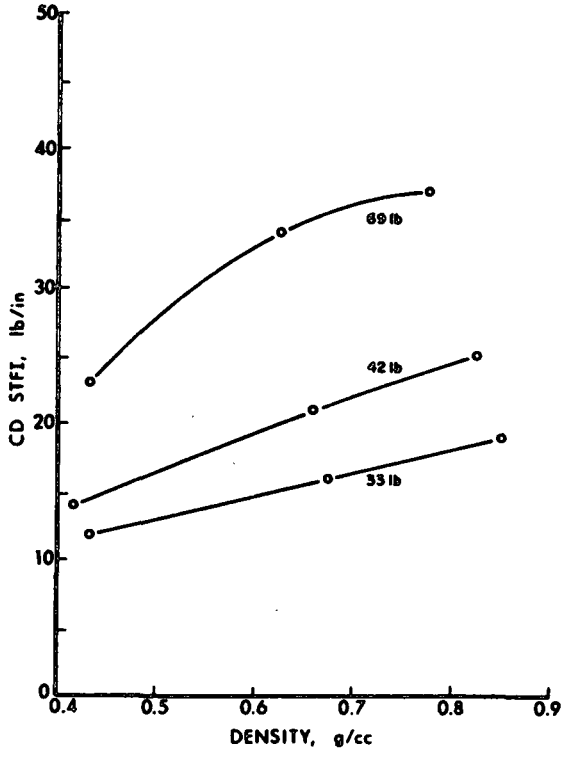


Figure 9. Variation of CD STFI with density.

Figure 13 shows that the geometric mean flexural stiffness results decreased with increasing density. As anticipated the variation in directionality had little influence on the geometric mean flexural stiffness. Thus the density and directionality changes had the planned effect of markedly changing the ratios of compressive strength to flexural stiffness. These variations for the 42-lb linerboards can be seen in Fig. 14 where we have plotted flexural stiffness versus CD STFI.

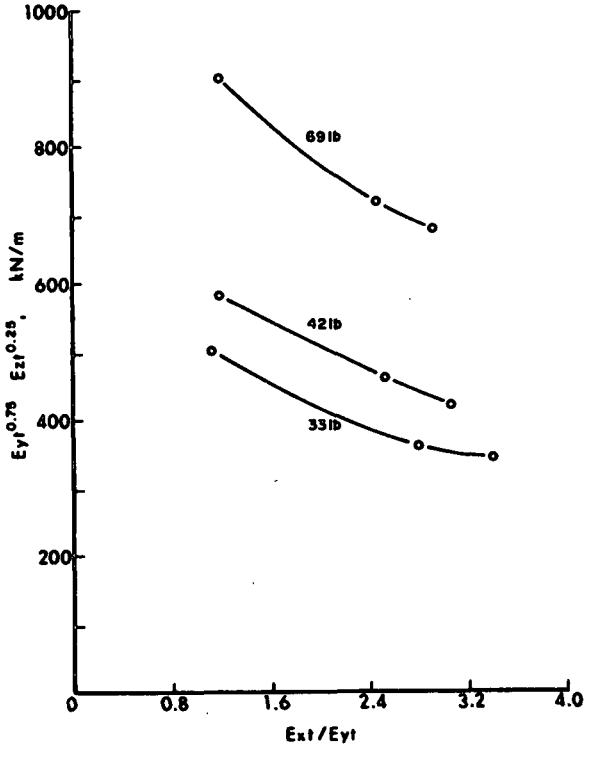


Figure 10. Variation of $E_yt^{0.75}$ $E_zt^{0.25}$ with density.

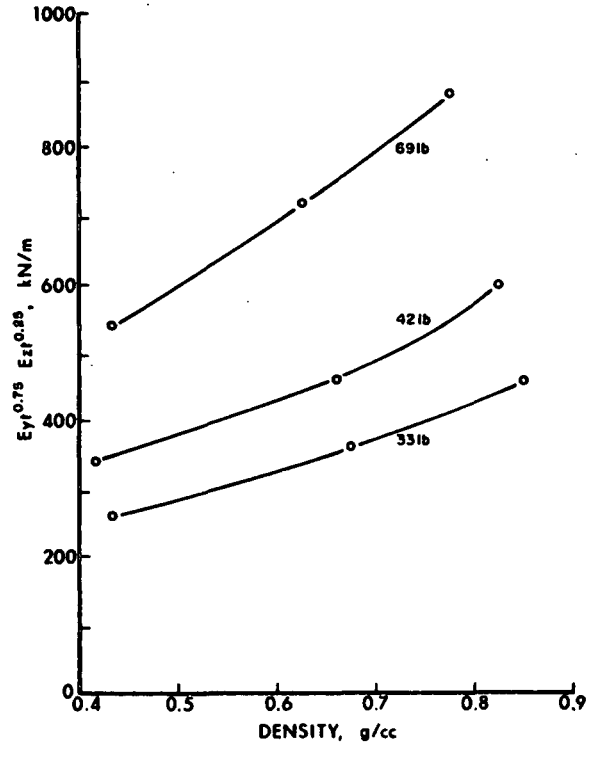


Figure 11. Variation of $E_yt^{0.75}$ $E_zt^{0.25}$ with directionality.

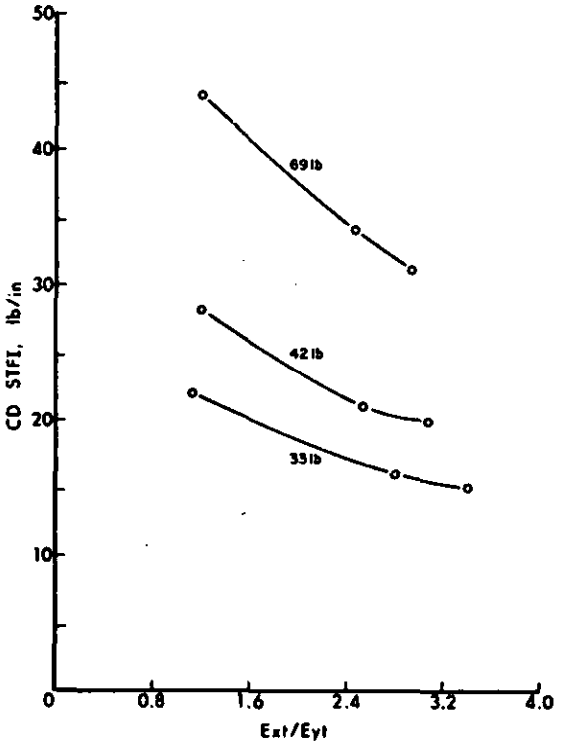


Figure 12. Variation of CD STFI with directionality.

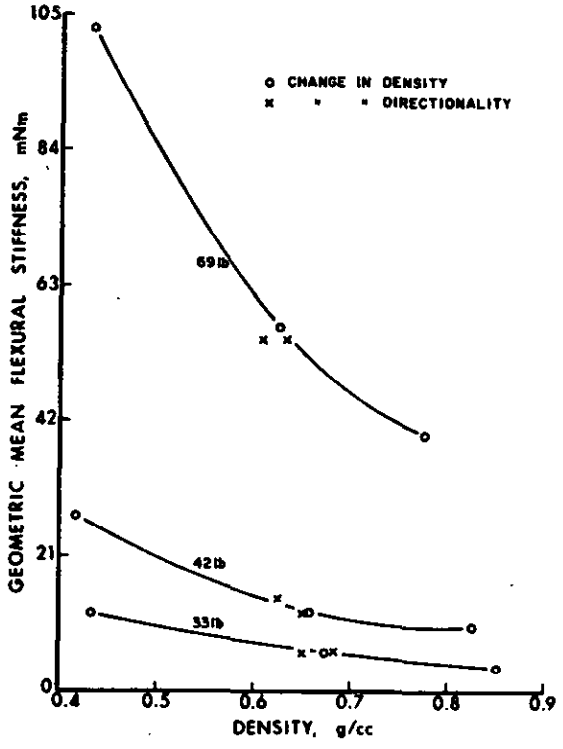


Figure 13. Variation of geometrical mean flexural stiffness with density.

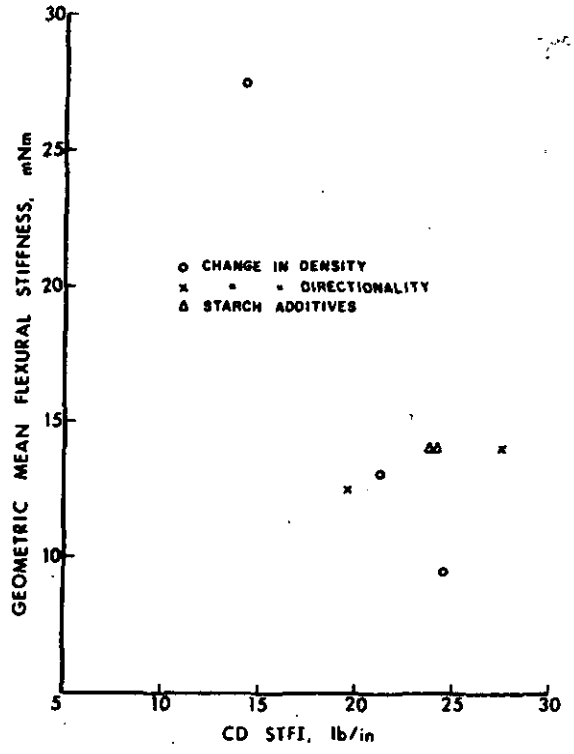


Figure 14. Variation of geometrical mean flexural stiffness with CD STFI.

We also examined the influence of internal strength additives in this study. Linerboards were made with two levels of starch additives for both the 33-lb and 42-lb weights. Figure 15 shows that the CD STFI increased with addition of starch while the geometric mean flexural stiffness was less affected. Figure 14 which shows flexural stiffness versus CD STFI for the 42-lb linerboards includes those with starch additives.

Our compressive model expression $E_y t^{0.75}$ $E_z t^{0.25}$ has been plotted against CD STFI for all the linerboards in this study in Fig. 16. The compressive stiffness model function is well related to STFI strength for all the papermaking variations.

These linerboard have been made into combined board using a 26-lb semichemical medium. ECT tests are in progress.

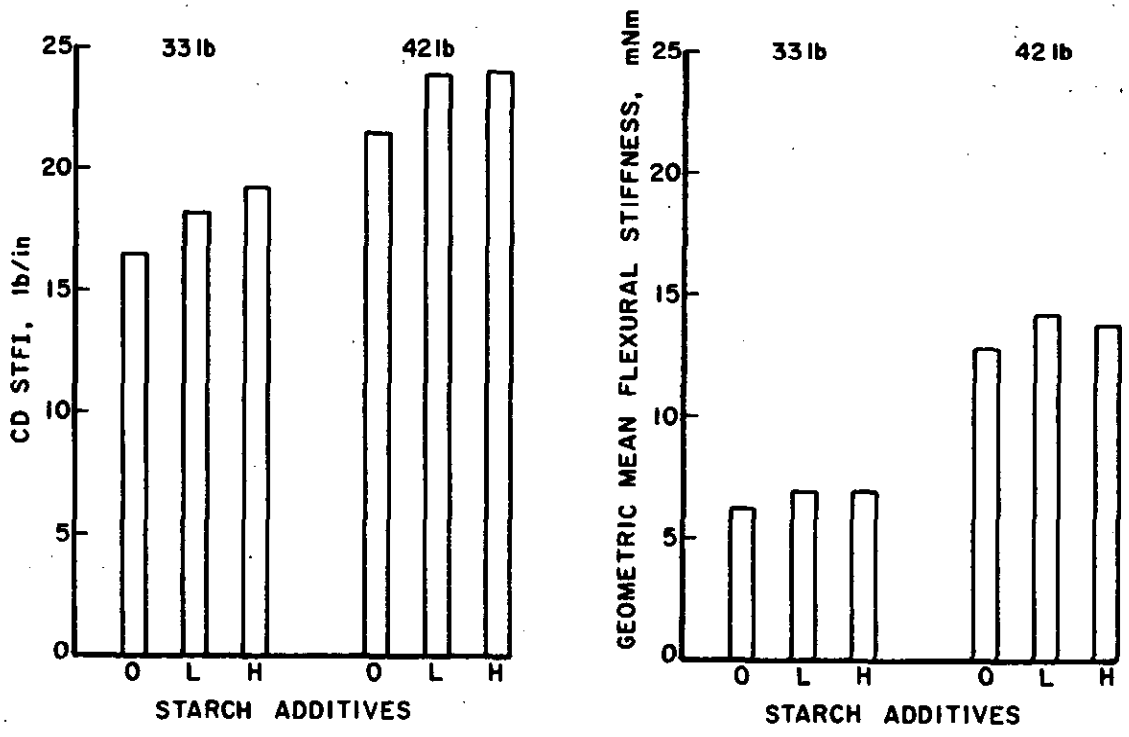


Figure 15. Variation of CD STFI and geometrical mean flexural stiffness with starch additives.

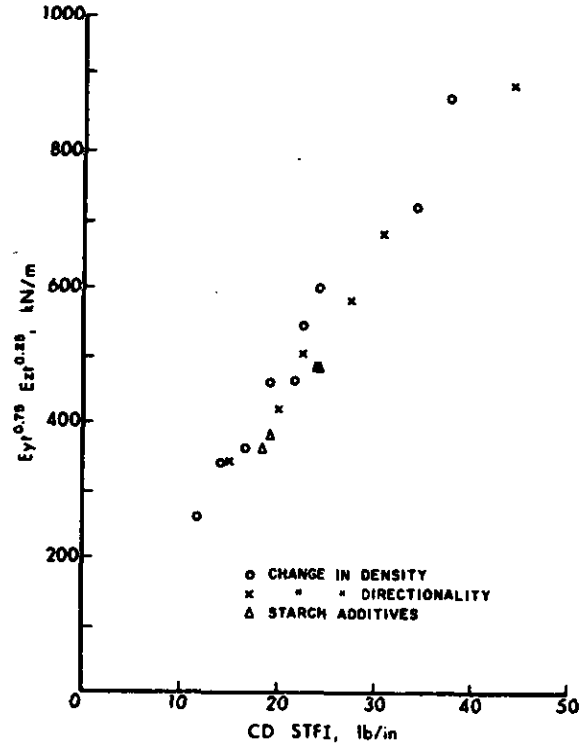


Figure 16. Variation of $E_y t^{0.75} E_z t^{0.25}$ with CD STFI.

FUTURE

Recently we reviewed our research plan for activity on this project. The following work is included in our plan.

A. ECT Modeling: Plan to complete in 1986

B. Component optimization for box compression strength. Expand work in A to evaluate the potential impact of papermaking changes in liner and medium on box compression.

C. Flat crush modeling. Use finite element techniques to show how medium properties affect the out-of-plane stiffness of combined board.

D. Corrugating medium improvement for strength retention. Develop information on other ways to improve retention. These include additives, directionality, formation and calendering.

E. Forming and bonding research: We need to expand and check our runnability models. This includes the following:

   a. Modeling: Consider strain-rate, moisture, temperature and compressibility effects.

   b. Finite element techniques to improve estimates of the bending strains during fluting.

   c. Forming geometry

During 1986 we plan work under subjects A, B, C, D and E.

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3500

COMBINED STRESS AND FAILURE PROCESSES

September 10, 1984

PROJECT SUMMARY

Date: 9/10/85
Budget: $60,000
Period Ends: 6/30/86
Project No: 3500

PROJECT TITLE: Combined Stress and Failure Processes

PROJECT STAFF: J. F. Waterhouse

PROGRAM GOAL:

Develop relationships between the critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

The objective is to improve methods for evaluating the in-plane and out-of-plane deformation behavior of paper and to relate these to end use performance, sheet composition and structure.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

(1) The effect of the severity of surface grinding on the measurment of in-plane and out-of-plane properties has been investigated.

(2) A brief investigation of the relationship of formation (MKS Formation Tester) and other sheet variables to tensile strength of commercial liner-board and medium has been made.

(3) An investigation of the effects of supercalendering on strength and other properties of coated and uncoated papers is in progress.

(4) The Hertel laboratory calender and supercalender has been relocated and is once again operational.

(5) A seminar on "Paper Properties, Terminology and Effects on Web Control" was given at a meeting organized by Rockwell International on Printing Press Web Control, February 19, 1985, Chicago.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

(1) A review paper on "Converting and Paper Properties" has been prepared and presented at the Tappi Plastics, Polymers and Laminations meeting in Chicago September 8. A copy of this is attached as Appendix I.

(2) A paper on "Z-direction variation of internal stress and properties in paper" has been prepared and will be presented at the Japanese Tappi/CPPA Tech. Sect. Paper Technology Meeting in Tokyo, Japan on October 17, 1985. A copy of this is attached as Appendix II.

(3) In student related work Laurine Charles is investigating the effects of supercalendering on the strength related properties of paper and board.

PROJECT TITLE: Combined Stress and Failure Processes (Formerly Shear Deformation and Failure)

PROJECT STAFF: J. F. Waterhouse

PRIMARY AREA OF INDUSTRY NEED: Properties related to end uses

PROGRAM AREA: Performance and properties of paper and board

Date: 6/1/85
Budget: $60,000
Period Ends: 6/30/86
Project No: 3500
Approved by V-R:

PROGRAM GOAL:

Develop relationships between critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

The objective is to improve methods for evaluating the in-plane and out-of-plane deformation behavior of paper and to relate these to end use performance, sheet composition and structure.

PROJECT RATIONALE:

We believe that both in-plane and out-of-plane properties are important to such converting processes as corrugating, molding, creasing, scoring and other forms of out-of-plane shape modification. Many converting operations involve combined in-plane and out-of-plane stresses (e.g., shear and bending) beyond the elastic regime. Successful converting depends on the sheet's ability to withstand such stresses. Research is needed to identify the critical stresses and the mechanism of failure. We wish to understand how the choice and location of materials in the web, and the papermaking process, affects paper properties, and to what extent they can be controlled to enhance converting performance.

RESULTS TO DATE:

Investigated methods for measuring the stress-strain shear behavior in the out-of-plane direction. Developed torsion mode technique for measuring shear. Studied effect of ZD shear straining on compressive strength. Internal stress variations have been determined in the thickness direction of paper together with the variation of in-plane and out-of-plane properties. A study has also been made on the effects of surface grinding variables on both in-plane and out-of-plane property measurements.

PLANNED ACTIVITY FOR THE PERIOD:

1) Explore methods for measuring combined stress deformation behavior.

2) Determine the effect of raw material and process variables on both in-plane and out-of-plane properties in the thickness direction of paper.

STUDENT RELATED RESEARCH:

L. Charles, M.S.-1986

Status Report

COMBINED STRESS AND FAILURE PROCESSES

Project 3500

Following the development of a method for measuring the out-of-plane shear deformation behavior of paper and board the effects of shear deformation on compressive strength were briefly examined, and surprisingly no significant adverse effects were found. During the development of the method for measuring out-of-plane shear deformation behavior (an important mode arising in many converting operations) ultrasonic characterization of the samples was also performed both in-plane and out-of-plane in the thickness direction of the board samples. This involved the symmetrical removal of material from the samples using surface grinding techniques, and in some cases machining them on a lathe. These measurements revealed some interesting variations of properties in the thickness direction, which have yet to be fully accounted for. As a consequence of these findings an investigation was made to determine the variation of drying (internal stress) stress in the thickness direction of paper. Both direct and indirect methods were used to determine this stress.

Stress relaxation was one method used to determine internal stress, on both commercial linerboard and press dried handsheets, a significant variation of internal stress in the thickness direction of paper was found. An alternative determination of internal stress was also developed using curvature and ultrasonic elastic property measurements. Two papers associated with these internal stress measurements and their possible consequences for some converting operations have been prepared, and are given in Appendix I and II of this report.

It is clear that in many converting operations paper and board are subjected to combined stress situations. Our intention is to investigate the process, and also to develop methods for measuring the response of paper and board

when subjected to combined out-of-plane stress situations. In student related work Laurine Charles is investigating the effects of supercalendering on the strength related properties of paper and board. This is one important converting process where paper is subject to complex combined out-of-plane stresses.

APPENDIX I

PAPER PROPERTIES AND CONVERTING

John F. Waterhouse
The Institute of Paper Chemistry
Appleton, WI 54912

INTRODUCTION

Paper and board in recent years have gained recognition as challenging engineering materials whose full potential has yet to be realized. This recognition stems from a more fundamental but as yet incomplete appreciation of the structure and properties of paper and board and the great diversity of products derived from them.

Understandably, paper and board product growth has been greater than the acquisition of the fundamentals necessary to optimize their performance for converting and end-use applications. One consequence of this has been the development of numerous test methods purportedly related to converting and end-use requirements. Ideally, we would like to be able to completely characterize our papermaking raw materials with the minimum number of variables and then use this information together with our understanding of papermaking technology to design a product to meet certain converting and end-use requirements. This approach underlines another difficulty and a real need, irrespective of what our design strategy may be, and it is that of understanding and specifying the correct "environment" which our paper and board products may be subjected to during converting and end-use. The published papers devoted to understanding the "environment" to which paper and board are subjected to during converting and end-use are few in number. Nevertheless, in strength related requirements, for example, it is clear that paper and board are more likely to be subjected to complex combined stress situations than a simple tensile stress. A further complicating factor in dynamic situations is an appreciation of the viscoelastic nature of paper and board.

This report will therefore be concerned with some paper property related needs of converting.

Converting and Paper Properties

Converting processes are many and varied as are the paper and board property requirements associated with them. However, they do have more in common than is perhaps realized. Some of the main areas of converting (1,2), are given in the table below.

Table 1 Converting processes

1.	Coating
2.	Calendering and Supercalendering
3.	Forming and Molding
4.	Laminating
5.	Impregnation
6.	Modification of Deformation Behavior
7.	Gluing, Bonding, Jointing
8.	Printing
9.	Size Reduction

In broad terms a base paper may be combined with other materials and subjected to one or more converting processes to produce a finished paper product. In general, converting processes are usually off the paper machine, i.e., "off-machine", but this is not always the case. For example, supercalendering is usually an off-machine process, but recently there has been renewed interest in on-machine supercalendering (3). Some of the more important paper property categories associated with the above converting processes are given in Table 2 below.

Table 2 Paper properties important to converting

- Deformation Behavior
- Dimensional Stability
- Wetting and Liquid Penetration
- Surface Characteristics

In what follows we will be mainly concerned with the deformation behavior and dimensional stability aspects of paper and the needs of converting.

Deformation Behavior

Paper is a network structure of fibers of finite length. This distinguishes paper from other foil-like materials. In some instances it is useful to treat paper as an anisotropic continuum, and to further simplify its description we can to a good approximation assume that paper can be represented as an orthotropic plate. A complete description of the elastic behavior of an orthotropic plate requires the measurement of nine elastic constants. These can be most conveniently measured using ultrasonic wave propagation techniques (4,5). In many instances an excellent correlation has been found between elastic properties measured nondestructively and failure properties (6). This is particularly valuable where one is contemplating the on-line measurement of a strength related property. When such on-line equipment becomes available commercially it may, in addition to the paper machine, find converting process applications.

Paper deformation behavior is in general controlled by network, fiber, interfiber bonds, and additive properties as shown in Fig. 1.

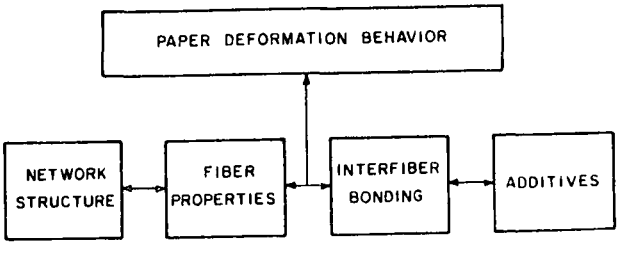


Fig. 1 Paper deformation behavior.

Considerable effort has been devoted to understanding the deformation behavior of paper and board, but until recently has been concentrated on the uniaxial tensile deformation behavior. In reality paper and board are subjected to more complex stress situations. Work is ongoing at a number of laboratories in the U.S.A. and elsewhere

to better understand deformation behavior when paper and board are subjected to combined stress situations including tension, compression, and shear (7,8). The familiar burst test is one example of a combined stress situation.

The above remarks have focused mainly on the in-plane deformation mode. However, the importance of the out-of-plane deformation mode is now beginning to be more fully appreciated. Out-of-plane deformation measurements are not readily made by mechanical means, although both the tensile (9,10) and shear modes (11-13) have been investigated using this approach. Again, as mentioned above, it is relatively easy to measure the out-of-plane elastic constants using ultrasonic wave propagation techniques. It is also interesting to note that some paper and board properties are directly dependent on both in-plane and out-of-plane properties, e.g., compressive strength. It may be anticipated that certain converting processes will not only depend upon, but may also modify the in-plane and out-of-plane properties of paper and board.

The viscoelastic nature of paper and board is another important factor which needs to be more fully appreciated in converting. Deformation behavior, for example, is dependent upon the time scale of loading. The time scale of laboratory testing is not always appropriate to many converting processes. Cellulose, at the molecular level, may be viewed as being comprised of ordered and less ordered regions. The less ordered or amorphous regions, which may be comprised of hemicelluloses, lignin, and cellulose, are mainly responsible for the viscoelastic nature of cellulose. An amorphous polymer is characterized by a well defined transition zone between its behavior as a glassy polymer and a rubbery polymer. For many polymers this well defined transition zone is usually denoted by a glass transition temperature. In the case of cellulose the transition zone is considerably broader, and the term softening temperature is preferred. Dry cellulose, hemicelluloses and lignin have softening temperatures of 230°C, 150-220°C, and 124-193°C, respectively (14) and in the absence of moisture, a very effective plasticizer, would exhibit glasslike behavior at room temperature. The deformation behavior of paper as a function of moisture content, will in part be determined by the amount of amorphous material present (when evaluated at constant temperature and humidity). However, if the moisture content is recalculated on the basis of the amount of amorphous material present, then the elastic properties as shown by Salmen (14), in Fig. 2 will essentially collapse onto a common curve. The amorphous content of a pulp may be changed by the type of species, pulping and bleaching process employed. Page (14a) has recently proposed that the difference in the behavior of sulfite and sulfate pulps may be attributable to differences in their viscoelastic nature.

So far we have reviewed the general nature of the deformation behavior of paper and board, and emphasized the importance of the out-of-plane mode. The deformation experienced by paper and board during converting operations, however, is not easily defined. It is apparent that failure, permanent set, and deformation modification mechanisms are involved, to some extent, in all of them and will be discussed in more detail below.

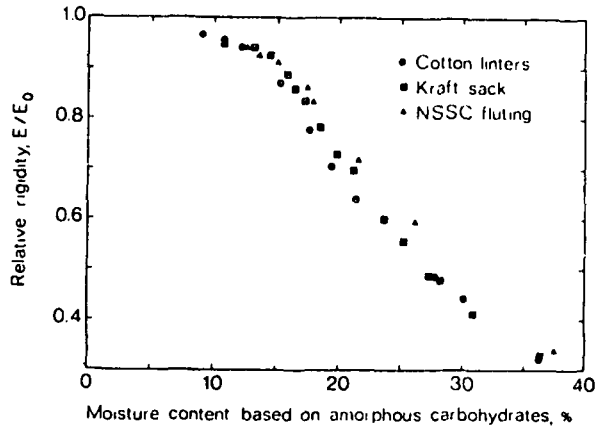


Fig. 2 Relative rigidity as a function of moisture content. Data of Salmen (14).

One important aspect of the runnability requirements of many converting processes is the ability of the web to withstand failure. In many instances the speed or productivity of the system may be limited by web breaks (e.g., newsprint) or by partial or total failure (e.g., flute fracture in corrugating). In web failure related runnability problems it is important to determine the nature of the loading.

Simplistically, in strength related runnability problems, failure will occur when the web loading exceeds the web's ability to carry a load. The applied loading is stochastic and it is usually not an easy matter to determine if the failure is a nonrandom event. This could be an important consideration, for example, when evaluating newsprint from different vendor sources.

The mode of failure is also not easy to define. In well run press rooms there is usually good documentation as to the category and causes of web breaks when some identifiable defect is present such as a shive or calender cut. The importance of shives has been investigated by Sears and coworkers (15), who found in laboratory runnability newsprint trials that shives were present in about 98.5% of the breaks. It is also interesting to note that the failures occurred at about only 20% of the web's tensile failure strain.

Using a fracture mechanics approach, Page and Seth (16) have established procedures for the measurement of fracture resistance of webs. Using this technique they have demonstrated, albeit with fifteen months of data collection, a correlation between runnability and fracture resistance. The process of fracture initiation in unflawed webs has received virtually no attention in the literature. This may be considered to be an extremely rare event but would certainly be part of the tally of breaks in a press room ascribed to unidentifiable sources. For example, it might be expected that sheet formation, i.e., small scale mass distribution variations, might play a vital role in runnability. This aspect has received limited

attention to date and includes paper machine wet-end runnability (17) and the effects of calendering on newsprint strength(17a). The work of Moffatt and co-workers (17a) shows that in uncalendered newsprint the failure path is connected through areas of low basis weight, whereas commercially calendered newsprint is through high basis weight zones. They also demonstrate the importance of long fiber content and fiber orientation in these areas. There is also a continuing controversy (18) regarding the appropriateness of certain tear measurements, i.e., Elmendorf vs. in-plane with respect to runnability.

Page and Seth (16) have also pointed out another important aspect of runnability, namely, seasonal variations, with peaks in break frequency occurring during the winter months. In press rooms which are not air-conditioned this behavior would be attributed to the viscoelastic nature of paper, i.e., it is expected that fracture resistance would decrease with decreasing moisture content. However, I am not aware of any results which have been published to substantiate this expectation.

Another example of a failure related runnability problem which has already been mentioned above is associated with the flute fracture of corrugating medium. The stresses to which the medium is subjected during the flute forming process are quite complex and include tensile, bending, shear, and compressive stresses. Other variables affecting the viscoelastic behavior which also have to be accounted for include moisture and temperature changes due to preconditioning. This author is not aware of any fundamental work which has been published in the area of failure under combined in-plane and out-of-plane dynamic loading, although there is clearly a need.

During a forming or molding operation the ability to retain shape is an important runnability consideration. Examples of converting operations where shape retention is important include corrugating, paper plate manufacture, pleating and embossing. Lack of desired shape retention can give rise to poor product performance such as in corrugating where "fluff out" contributes to highs and lows.

In order to retain shape, paper or board must undergo some degree of permanent set during forming or molding. Again the material will be subjected to a complex stress situation and loss of the formed shape will occur due to elastic recovery and relaxation effects, unless the material is perfectly plastic. As a simple illustration, consider the case of forming a segment of paper or board of thickness t to a radius R_i (where R_i is the radius at the neutral axis). It can easily be shown that the applied strain ε_i at $y = \alpha t$ (i.e., at the outermost fiber layer) is given by:

$$\varepsilon_i = \frac{\alpha t}{R_i} \qquad (1)$$

If the cross section of the paper segment is symmetrical both with respect to geometry and elastic properties, and there are no external forces applied to the segment, then the neutral axis will coincide with the geometric axis, e.g., for a rectangular cross section $\alpha = 1/2$. After release from the mold the final radius R_f will be given by an expression similar to Eq. (1), i.e.,

$$\varepsilon_f = \frac{\alpha_f t_f}{R_f} \qquad (2)$$

where ε_f now represents the amount of permanent set after initial elastic recovery and stress relaxation and α_f accounts for any change which might occur in the position of the neutral axis. We also note that the final caliper t_f may differ from the initial caliper, since in many forming processes the paper or board will also be subjected to compressive stresses and therefore undergo some permanent set in this deformation mode. If we define the amount of spring back S as

$$S = R_f/R_i - 1 \qquad (3)$$

then from the above equations we have;

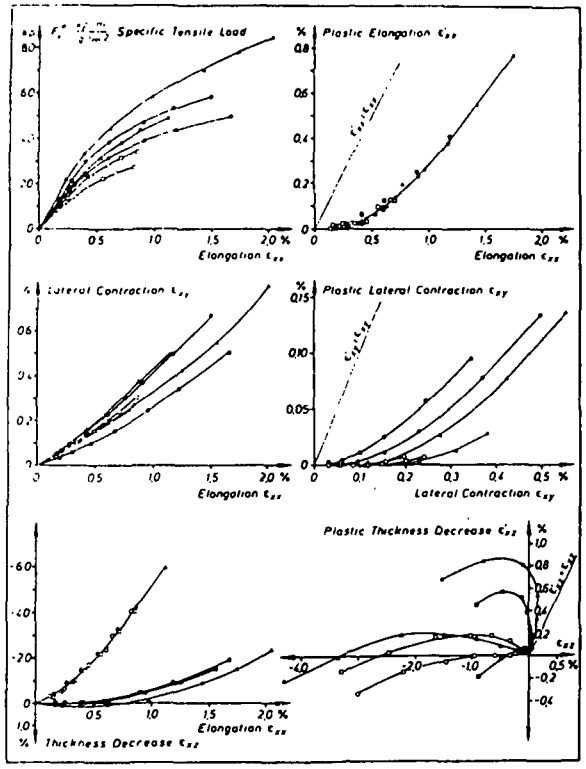
$$S = \frac{\alpha_f}{\alpha}\frac{\varepsilon_i}{\varepsilon_f}\frac{t_f}{t} \qquad (4)$$

In order to estimate the spring back S we need to know the relationship between the amount of permanent set ε_f and initial elongation ε_i in the tensile deformation mode.

It has been shown by a number of workers (19, 20) that the relationship between ε_f and ε_i is to a good approximation independent of species, pulping type and beating for wood fibers as shown in Fig. 3. However, if the fibers are highly curled and microcompressed, then this relationship may be altered (20). If synthetic fibers (20) are incorporated into the sheet or if the foil material is different, the relationship again will change as shown in Fig. 4. It is interesting to note in Fig. 4 that the aluminum foil behaves almost as a perfect plastic. Differences in permanent set behavior may be important when forming or molding laminates of different materials. This author is unaware of any published work which examines the influence of temperature, moisture and strain rate on the set characteristics of paper and board.

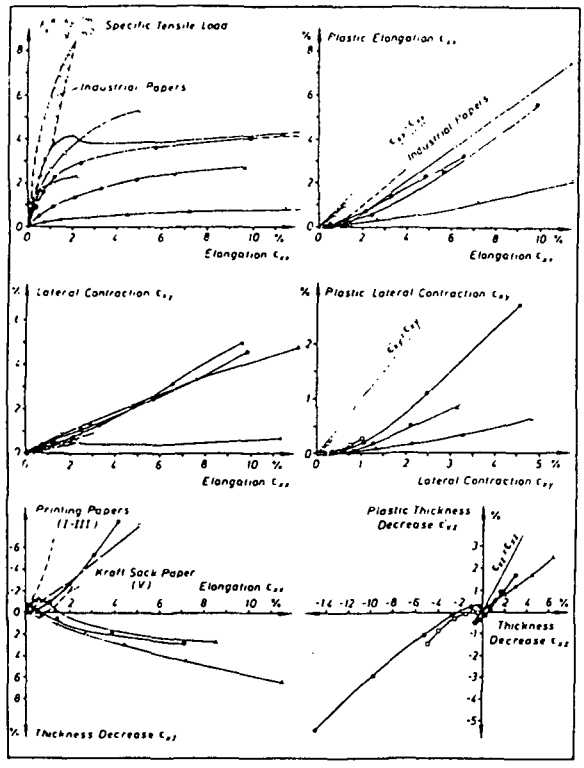
In converting there are some specific paper properties we deliberately try to improve (e.g., in supercalendering smoothness and gloss), however, they may be accompanied by losses in other properties. It is believed that with a better understanding of the process, these losses can not only be minimized, but these same properties enhanced. To illustrate this point strength changes as a function of calendering and supercalendering (21) are given in Table 3.

The data illustrate that properties may suffer a loss, remain unaltered, or be enhanced. The reasons for this range of behavior are not well understood. We know that in supercalendering the paper is subjected to a complex combined stress situation, including out-of-plane cyclic shear and compressive stresses, at elevated temperatures. The effect of these stresses on paper properties has yet to be determined. Crotogino (22) has sought to minimize the effects of calendering on paper property degradation. He has limited the calendering effect to the surface of the sheet in a process called "temperature gradient" calendering.



—Deformations in tensile tests with straining cycles
Industrial papers (machine-direction)
⊃ Uncoated illustration printing paper (I)
△ Coated illustration printing paper (II)
⊐ Newsprint paper (III)
● Offset printing paper (IV)
▲ Kraft sack paper (V)
■ Folding boxboard (VI)

Fig. 3 Data of Gottsching and Baumgarten (19).



Deformations in tensile tests with straining cycles packaging foils and printing substrates (machine-direction)
⊃ Aluminium packaging foil (XI)
△ Polythene packaging foil (XII)
⊐ Printing paper from synthetic fibres (XIII)
● Printing paper from synthetic fibres (XIV)
▲ Polystyrene printing foil (XV)
■ Polythene printing foil (XVI)

Fig. 4 Data of Gottsching and Baumgarten (19).

Table 3 Effects of calendering and supercalendering on the strength properties of some grades of paper. Data of Rance (21).

Calender Grade	Newsprint		Rotary Print		6-ply Board	
	Before	After	Before	After	Before	After
Grammage, g/m^2	54		52			
Density, g/cm^3	0.376	0.549	0.535	0.709	0.556	0.680
Breaking Length (km)	4.8	5.0	3.8	3.3	5.6	6.0
Tear MD (mN)	23	19.5	48	39		

Supercalender Grade	Newsprint		Machine Coated		Glassine	
	Before	After	Before	After	Before	After
Grammage, g/m^2	54		105		32	
Density, g/cm^3	0.408	0.633	0.909	1.163	0.8	1.316
Breaking Length (km)	2.2	2.2	4.6	1.1	1.1	1.3
Tear MD (mN)	19	16	55	47	17	15

The fluting of medium is an example where significant compressive strength losses are incurred during forming. The complex stresses involved have already been referred to above. Whitsitt (23) has demonstrated that bending stresses are mainly responsible for these losses. This author (13) has investigated the role of shear deformation, another important forming stress, on compressive strength and found no significant changes.

Dimensional Stability

Dimensional stability is an important problem often encountered in the converting and end-use properties of paper and board. The papermaker strives hard to minimize subsequent dimensional stability problems, but in spite of his best efforts they still arise. The converters approach to dimensional stability problems will of necessity be different from the papermakers.

Dimensional stability is concerned with changes in the dimensions of paper and board when subjected to a change in their environment, for example, moisture, temperature, stress or some combination thereof. Moisture or moisture related dimensional changes are usually the most important. Planar dimensional stability is very critical in most printing processes, particularly multicolor processes where register is of paramount importance. In machine-made papers the thickness direction is the least stable, usually followed by the cross machine and machine directions, respectively.

In this brief review, our main concern will be with a particular dimensional stability problem called curl, or in the case of combined board,

warp. Curl or warp, in addition to being unacceptable from an aesthetics point of view, are the prime causes of many runnability problems. They also affect end-use performance. The base stock may be essentially curl free, but unacceptable curl characteristics may develop in subsequent converting operations. An added complication is that the curl may be time dependent. Curl is basically associated with property nonuniformities from plane to plane in the thickness direction of paper or board (more generally known as two sidedness). These potential nonuniformities can arise from many different sources in the papermaking process. Although they can be controlled, it is unlikely they can be completely eliminated. Even with materials which are dimensionally stable with respect to moisture changes (low hygroexpansivity), curl can be induced during converting operations, such as coating and laminating, due to differential thermal shrinkage of the components. Much has been written on the subject of dimensional stability and curl, and the interested reader is referred to the surveys by Gallay (24,25), Green (26), and Rutland (27).

There are two basic types of curl: reversible curl and irreversible curl. Ideally, one would like to be able to monitor the curl potential of a substrate so that during converting, strategies can be adopted in order to correct for the likelihood of induced curl in such a way as to minimize any adverse effects on paper properties.

In what are now regarded as classical experiments, Page and Tydeman (28) deduced that the amount of shrinkage which occurs during the unrestrained drying of paper must be attributed to lateral shrinkage of the fiber. From geometrical arguments the fibers in the dried sheet had to be shorter than those in the wet sheet. They established that the lateral shrinkage of an isolated fiber is considerably greater than the shrinkage along its axis. The axial shrinkage is negligible compared to that which must be experienced by the fibers in a freely dried sheet. Therefore, the shortening of the fibers in the sheet must be the result of interfiber bonds. The lateral shrinkage of one fiber induces longitudinal shrinkage in the fiber to which it is bonded.

Surprisingly little data have been published on the lateral shrinkage or expansivity behavior of papermaking fibers. Page and Tydeman (29) used direct measurements to show that the lateral shrinkage of fibers could vary widely, but was moderately increased by refining. The differences between bleached spruce sulfite and unbleached pine sulfate cooks were small. It was also found that lateral shrinkage was not completely reversible upon rewetting the fiber.

Another novel technique for measuring the lateral hygroexpansivity of single fibers was developed by Mark (30). It basically consists of measuring the angular torsional displacement of a fiber when its moisture content is changed. This displacement will also be a function of fibril angle. deRuvo and co-workers (31) used this technique and found that the twist angle was a linear function of moisture regain, up to relative humidities in excess of 80%.

The amount of shrinkage which a freely dried paper undergoes will depend on the extent to which the lateral shrinkage potential of the fibers is realized through interfiber bonding. Therefore, both refining and wet pressing will be effective in this respect.

The dimensional changes which occur when paper is subjected to humidity changes will also depend on the level of restraint or the amount of shrinkage which has taken place during drying. The greater the shrinkage, the greater the subsequent dimensional change of the sheet. It is proposed [following a similar argument by Corte (32)] that humidity changes will mainly produce a lateral expansion in the fiber cross section, and the resistance to this expansion will in part be controlled by the effective fiber modulus at the interfiber bond. The lower the effective restraint during drying, the greater the induced "shrinkage" and the lower the effective fiber modulus at the interfiber bond. Thus, a freely dried sheet will be less dimensionally stable than one dried under restraint or wet strained. As an aside, it should also be realized that the extent of interfiber bonding for a given level of wet pressing will also increase with increasing sheet shrinkage during drying. This is illustrated in Fig. 5 where a typical variation of apparent density* (which is used as a measure of bonding) with drying restraint is shown.

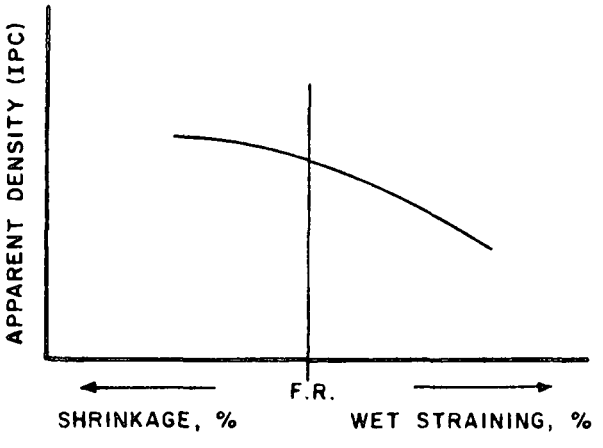


Fig. 5 Variation of apparent density with drying restraint.

Machine made papers are invariably less dimensionally stable in the cross machine direction and this is further exacerbated by increasing MD fiber orientation. It should be emphasized, however, following Wink (33), Back (34) and others, that dimensional changes depend on the range, particularly the upper limit, of humidity used. It is possible with high levels of wet straining, that MD changes will be greater than CD changes if the humidity change is not too great (34). Again we should remind ourselves that curl may be partly reversible and partly irreversible.

*The apparent density is calculated using soft platen caliper measurements (35).

Carlsson (36) and co-workers have analyzed the reversible curl problem using elastic lamination theory and a linear relationship between the coefficient of hygroexpansion and moisture content H. Their result for the curvature K of a two layer laminate, when exposed to a uniform change in moisture content, where 1 and 2 might represent the wire and felt sides, is given as follows:

$$K = \frac{1}{R} = \frac{24\ (\beta_2 H_2 - \beta_1 H_1)}{t(E_1/E_2 + E_2/E_1 + 14)}$$

E_1, E_2 and t are the respective moduli and sheet thickness. The coefficients of hygroexpansion, β_1 and β_2, will depend on the type of pulp, level of refining, wet pressing and fiber orientation pertaining to that layer. The prediction appears to work quite well for the humidity range where reversible curl is expected, i.e., less than about 65% RH. Above this RH (or critical moisture content) relaxation effects and irreversible curl have to be accounted for.

Internal or residual stresses are established in paper and board during the drying process. The modification of these by externally applied stresses, or the relaxation of them by moisture, temperature or some combination of the above, will produce a permanent or irreversible dimensional change. Johanson and co-workers (37) demonstrated the relationship between internal stress and dimensional stability. Internal stress was determined using stress relaxation measurements, and it was shown that moisture treatment of the samples reduced the level of internal stress and dimensional stability, while the application of an external cyclic stress increased the level of internal stress and dimensional stability. A further interesting finding was that a combination of external stress and moisture treatment resulted in a greater relaxation of internal stress and reduction in dimensional stability than a moisture treatment alone! It has also been shown by Htun (38), employing a relaxation technique developed by Johanson and co-workers (37), that the level of internal stress is equal in magnitude to the drying stress. Relevant to the problem of curl and other paper properties is the distribution of this internal stress in the thickness direction. Under equilibrium conditions there is no resultant stress acting on the paper. This implies that the internal stress is a balance between compressive and tensile stresses as shown in Fig. 6.

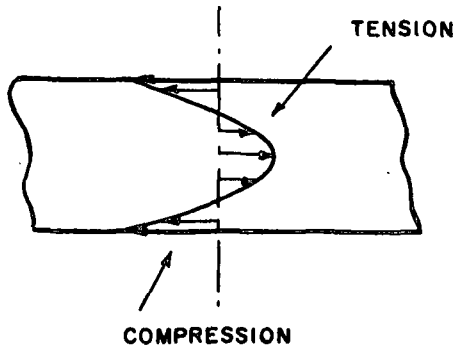


Fig. 6 Internal stress distribution of paper.

Direct evidence for the existence of internal stresses and alternative methods of measurement has been sought by this author. Using a surface grinding technique, developed by Wink (39) and Beckman (40), a 42-lb linerboard sample was surface ground to produce felt, middle and wire side sections. The properties of these are given in Table 4. The significant changes in curvature of these sections, particularly the felt and wire sections, are shown in Fig. 7. These are attributed to the release of internal stress. Indeed it can be shown that curvature measurements on these sections, together with measured elastic properties, can be used to estimate the internal stress distribution.

Table 4 Properties of surface ground sections.

Sample	BW, g/m^2	IPC Cal., mm	Density, g/cm^3	E/ρ MD $(km/sec)^2$	E/ρ CD $(km/sec)^2$	R	E_z/ρ $(km/sec)^2$
Felt	94.1	0.1219	0.772	12.43	5.19	2.39	0.0692
SD				0.426	0.263		
Middle	98.7	0.1358	0.727	11.43	5.04	2.27	0.0428
SD				0.765	0.263		
Wire	86.9	0.1191	0.729	12.09	3.81	3.17	0.0595
SD				0.608	0.281		
Whole sheet	207.5	0.287	0.723	13.1	6.23	2.10	0.0639

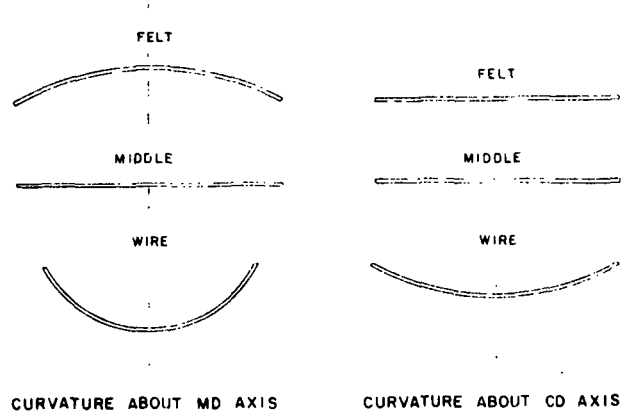


Fig. 7 Curvature measurement on the felt, middle and wire sections of 42-lb linerboard.

An ideal paper, i.e., one which has uniform composition, fiber orientation and bonding at any plane in the thickness direction, will also have an internal stress distribution similar to that shown in Fig. 6. The magnitude of the stresses will be dependent on the drying rate, since paper is a viscoelastic material. The effect of drying rate on the level of internal stress has also been studied by Htun (41). It is interesting to note that internal stress development in other viscoelastic materials, is vital to their properties. Examples include the thermal toughening of glass, the kiln drying of wood, and the processing of plastics.

Therefore, if the internal stress distribution of paper or board is altered by some means, e.g., moisture, temperature, or externally applied stresses, their curvature must also change. We can

therefore refer to curl as a manifestation of internal stress changes. Again it should be noted that this type of curl is permanent.

SUMMARY

Certain paper property needs of converting, namely, deformation behavior and dimensional stability have been the subject of this review. The anisotropic and viscoelastic nature of paper, and the growing importance of out-of-plane properties is emphasized. The possibility of measuring both in-plane and out-of-plane elastic properties using ultrasonic wave propagation techniques is considered as a possible future application for converting. Other aspects of deformation behavior examined include strength related runnability problems, permanent set and the modification of paper properties.

The basic mechanisms controlling dimensional stability and curl are reviewed from the converter's point of view. Both reversible and irreversible curl are discussed, in particular, the relationship between the internal stress distribution in paper and irreversible curl. An appreciation of the mechanisms and types of curl should aid in the development of effective strategies for dealing with it in such a way as to minimize any adverse effects on other paper properties.

REFERENCES

1. Casey, J. P., Pulp and Paper, Chemistry and Technology, 3rd edn., Vol. 4, John Wiley and Sons, Inc., 1983.

2. Satas, D. Web processing and converting technology and equipment. Van Nostrand Reinhold Company Inc., 1984.

3. Ichinose, L. Y., PIMA, Dec., 1984, p. 34.

4. Mann, R. W., Baum, G. A., and Habeger, C. C. Tappi **62**(8): 115(1979).

5. Baum, G. A. The elastic properties of paper. Progress in paper physics seminar. Stockholm, June, 1984, To be published.

6. Baum, G. A. Paper **19**: 65, 67(March, 1984).

7. de Ruvo, A., Carlsson, L., and Fellers, C. Tappi **63**(5): 133(1980).

8. Gundersson, D. E., and Rowlands, R. E. Determining paperboard strength - Biaxial tension, compression and shear. Proceedings of the International Paper Physics Conference. TAPPI Press, 1983, p. 253.

9. Wink, W. A., and Van Eperen R. H., Tappi, **50**(8): 393(Aug., 1967).

10. Van Liew, G. P., Tappi, **57**(11): 121(Nov., 1974).

11. Byrd, V. L., Setterholm, V. C., and Wichmann, J. F., Tappi, **58**(10): 132(Oct., 1975).

12. Fellers, C., Svensk Papperstid., **3**(80): 89(1977).

13. Waterhouse, J. F., Tappi J., **67**: 6(1984).

14. Salmen, L. Temperature and water induced softening behavior of wood fiber based materials. Doctoral Thesis. Stockholm, Sweden. The Royal Institute of Technology. Dept. of Paper Technology, 1982.

14a. Page, D. H., J. Pulp Paper Sci., March, 1983, p. TR15.

15. Sears, G. R., Tyler, R. F., and Denzer, C. W., Pulp Paper Mag. Can., **66**(7): T351(July, 1965).

16. Page, D. H., and Seth, R. S., Tappi, **65**(8): 92(Aug., 1982).

17. Yang, C. F., and Thorpe, J., Tappi, **60**(12): 141(Dec., 1977).

17a. Moffatt, J. M., Beath, L. R., and Mihelich, W. G. Major factors governing newsprint strength. The fundamental properties of paper related to its end uses. Trans. of Symposium held at Cambridge, 1973.

18. Van den Akker, J. A., Wink, W. A., and Van Eperen, R. H., Notes to the editor. Tappi, **59**(11): 130(Nov. 1976).

19. Gottsching, L., Baumgarten, H. L. Triaxial deformation of paper under tensile load. The fundamental properties of paper related to its uses. Trans. of Symposium held at Cambridge, 1973.

20. Waterhouse, J. F., Tappi, **59**(7): 105(July, 1976).

21. Rance, H. F. Consolidation of the paper web, Chapter 5 Handbook of Paper Science Vol. 1 Edited by Rance, H. F. 1982 Elsevier, Publ.

22. Crotogino, R. H., Tappi J., 65(10): 97(Oct, 1982).

23. Whitsitt, W. J., and Sprague, C. Mechanics of fluting. Report One, Project 3396. The Institute of Paper Chemistry, Internal Report. (June 15, 1981).

24. Gallay, W., Tappi, **56**(11): 54(Nov., 1973).

25. Gallay, W., Tappi, **56**(12): 90(Dec., 1973).

26. Green J. G. Jr. Curl, expansivity, and dimensional stability. Chapter 27, Vol. 2 Handbook of physical and mechanical testing of paper and paperboard. Ed R. Mark. Marcel Dekker Inc., 1983.

27. Rutland, D. F. Dimensional stability and curl of papers. Proceedings of the C.P.P.A. 71st Annual Meeting, 1985.

28. Page, D. H., and Tydeman, P. A. Formation and structure of paper. Symposium F. Bolam Ed Tech. Section B.P.B.M.A. London, 1962.

29. Page, D. H., and Tydeman, P. A., Nature, 199: 471(Aug. 3, 1963).

30. Mark, R. E., Thorpe, J. L., Angello, A. J., Perkins, R. W., and Gillis, P. P., J. Polymer Sci., (C Polymer Symposium) **36**: 177(1971).

31. de Ruvo, A., Lundberg, R., Martin-lof, S., and Soremark, C. The influence of temperature and humidity on the elastic and expansional properties of paper and the constitutient fiber. The fundamental properties of paper related to its uses. Trans. of Symposium held at Cambridge, 1973.

32. Corte, H. Cellulose - Water Interactions. Chapter 1, Pg. 50, and 71. Handbook of Paper Science Vol. 1 Edited by Rance, H. F. 1982. Elsevier, Publ.

33. Wink, W. A., Tappi, **41**(6): 171A(June, 1961).

34. Back, E. L., and Klinga, L. O., Tappi, **46**(5): 284(May, 1963).

35. Wink, W. A., and Baum, G. A., Tappi J. **66**(9): 131(Sept., 1983).

36. Carlsson, L. A study of the bending properties of paper and their relation to the layered structure. Doctoral Dissertation, Chalmers University of Technology, Gothenberg, Sweden, 1980.

37. Johanson, F., Kubat, J., and Pattyranie, C., Svensk Papperstid. (10):333(May 31, 1967).

38. Htun, M., and de Ruvo, A. Relation between drying stresses and internal stresses and the mechanical properties of paper. Fiber - Water Interactions in Paper-Making. Trans. of the Symposium held at Oxford, Sept., 1977.

39. Wink, W. A., Private Communication.

40. Beckman, N. J., and Plucker, E. I. Z direction analyses of coated papers using large area sectioning techniques. TAPPI Coating Conference Preprint April 30-May 2, 1973.

41. Htun, M. The influence of drying time and temperature on drying stress and related mechanical properties of paper. Doctoral Dissertation. The Royal Institute of Technology, Stockholm, Sweden 1981.

APPENDIX II

Z-DIRECTION VARIATION OF INTERNAL STRESS AND PROPERTIES IN PAPER

J. Waterhouse, S. Stera and D. Brennan

The Institute of Paper Chemistry
Appleton, Wisconsin, U.S.A.

INTRODUCTION

There is a growing awareness of the importance of both in-plane and out-of-plane strength properties with respect to the converting and end-use requirements of paper. The in-plane strength properties of paper are relatively easy to measure mechanically, and recently, nondestructive ultrasonic wave propagation techniques have been developed to measure the elastic constants of paper (1). Out-of-plane properties are, by comparison, much more difficult to measure mechanically. There is still a need in this area for reliable and less time-consuming measurement techniques. Ultrasonic wave propagation techniques have also been developed to measure the out-of-plane elastic constants (2). One of the goals of nondestructive measurement techniques is to be able to predict both in-plane and out-of-plane failure and other strength related properties. A number of predictions have already been established, including tensile strength, compressive strength, and out-of-plane or z-direction tensile strength (3).

With the above goal in mind, Waterhouse (4) investigated the out-of-plane shear deformation behavior of paper employing a torsion mode. During the course of this investigation, where both mechanical and ultrasonic measurements were made, a significant variation in both in-plane and out-of-plane properties was found as material was symmetrically removed from linerboard and medium samples by surface grinding. The implication was that in-plane and out-of-plane elastic properties varied from plane to plane in the thickness direction. Furthermore, there was a difference (which has yet to be explained) in the variation of out-of-plane shear modulus in the thickness direction when measured mechanically and ultrasonically (4).

It is well known that paper is two sided, i.e., there is a felt and wire side. This arbitrary division is usually attributed to differences in fiber orientation and fines distribution within these regions. Less attention has been given as to how properties generally vary in the thickness direction and the factors controlling them. In addition to formation, wet pressing and drying conditions are possible factors which could influence property variations in the thickness direction. Further property modifications are possible during other operations, e.g., supercalendering. With regard to converting and end-use requirements, the most favorable distribution of properties in the thickness direction has yet to be determined.

One of the major difficulties which arises in determining the uniformity of composition or properties in the thickness direction is that of splitting or sectioning the sheet into layers. Parker and Mih (5) (who developed the Beloit sheet splitter), list various methods which have been used for this purpose, including razor blades, grinding, peeling with adhesive tape, and microtoming. In addition to the problem of obtaining uniform sections with minimal damage, there is concern that the properties of a particular section may be different from the properties of that same section in the whole sheet. The properties may change due to a release or change in internal stress. It is not expected that the sectioning process, and as a consequence changes in strength related properties, will have any effect on the composition of that section, i.e.,

filler, fines content, fiber orientation, or formation. Parker and Mih (5) used the Beloit sheet splitter to demonstrate among other things, ink penetration during printing, fines (filtration resistance) and filler (ash) distribution in the thickness direction. Fines distribution is clearly dependent on the type of forming method used. Parker and Mih (5) found that fines were more highly concentrated on the wire side of handsheets, whereas the maximum concentration of fines was on the felt side of fourdrinier produced paper. One disadvantage when using the Beloit sheet splitter is having to wet out the samples, since this precludes any meaningful measurements of strength related properties on the split sections. Mechanical properties on the redried sections would be different than in the original paper because of different drying conditions.

Kallmes (6) used the Beloit sheet splitter and IPC zero span tester to determine the z-direction variation of fiber orientation. He argued that the rewetting and drying of the samples should have a negligible effect on the MD/CD zero span ratio. Kallmes found, with a few exceptions, that the wire side of the sheet tends to be more square than the felt side of the sheet for both commercial sheets and those formed on an experimental former. In the experimental sheets it was also found that the greater the fiber orientation of the whole sheet, the greater the difference in orientation between the felt and wire sides of the sheet. Another interesting finding by Kallmes (6) on commercial sheets which had been split into four sections, was that fiber orientation was higher in the middle sections of the sheet. A similar effect was reported by Waterhouse (4), who found an increase in elastic modulus anisotropy in commercial linerboard and medium samples toward the middle of the sheet. It was suggested that the increase in anisotropy was due to variations in drying stress in the thickness direction, i.e., the interior layers of the sheet experienced a lower drying stress than the outer layers.

Wet pressing is an important process step in papermaking which serves not only to remove water from the web, but to consolidate it. Strength development through interfiber bonding is one of the main consequences of the consolidation process which is still not completely understood. Wickes (7) has demonstrated that interfiber bonding may not be uniform in the thickness direction. Using laminated wet webs and blotter stock as the wet press felt, he found a significant variation in both solids content and apparent density from layer to layer in the thickness direction. With two sided water removal, the distributions were still nonuniform but symmetrical. No results were reported for commercial wet press felts, and no other physical property measurements were made. It is also possible that nonuniformities in bonding from layer to layer in the thickness direction might be caused by internal damage due to too high a rate of water removal, in some instances giving rise to crush. Movement of fines and nonuniformities in the thickness direction during consolidation have been discussed by McGregor (8). He refers to this effect as sheet stratification, which he defines "as the change in vertical distribution of sheet fiber and filler material resulting from fluid shear force development during the dynamic wet pressing process". In summary we can say that wet pressing can influence the web structure in the following ways:

1) Uniformity of consolidation in the thickness direction
2) Stratification, i.e., movement of fiber and fines material due to fluid shear
3) Internal sheet disruption with excessive rates of water removal
4) Surface disruption dependent on felt type, press configuration and water removal rates

In the drying process water remaining mainly in the cell wall of the fibers is removed. This is accompanied by large changes in the dimensions of the fiber's cross section. These dimensional changes are communicated to other fibers in the network through interfiber bonding, and exert a considerable influence on the network's in-plane and out-of-plane deformation behavior, depending on the type of restraint applied during the drying process. In effect, the fiber's deformation behavior is modified, i.e., a sheet which is dried without restraint will

consist of fibers which are microcompressed, the extent of which will depend on the level of interfiber bonding. Differences in the machine and cross machine direction restraint conditions on a paper machine are well recognized as being, in part, responsible for the anisotropy in various sheet properties.

If the sheet is restrained during the drying process, it is possible to monitor the drying stress it experiences. Htun (9) and others have shown that the deformation behavior of the network can be correlated with drying stress. Using the stress relaxation technique first used by Johansson and Kubat (10) to measure internal stress in paper, Htun also showed that drying stress is equal to internal stress. He also demonstrated that the level of drying stress is dependent on the viscoelastic nature of paper, i.e., the deformation behavior will be dependent on the drying conditions.

Returning to our main consideration of property variations in the z-direction, it is possible that even with a web having uniform composition, fiber orientation, and bonding, there can still be variations in drying and internal stress and related physical properties in the z-direction. Htun (9) discussed various definitions of stress. In keeping with the broader perspectives of materials science it is recommended that residual stress or internal stress are the more fundamental terms we should employ for paper. The term residual stress appears to be the one most commonly employed in the literature. The level and variation of internal stress in other materials, e.g., glass, wood, plastics, metals, adhesives, are of considerable concern to material scientists. Techniques for the measurement of internal or residual stress include photoelasticity, ultrasonics (stress-acoustic effect and surface Raleigh waves), stress relaxation, hole drilling, x-ray diffraction, eddy current, and layer removal employing strain gage or curvature measurements. Some of these methods are nondestructive, while others are only applicable to specific materials.

The main objectives of the present work are to measure the variation of internal or residual stress and associated properties in the z-direction. An attempt has been made by Lindroos and Waterhouse (11), to directly measure the variation of drying stress in the z-direction, and we hope to report on those results elsewhere.

RESULTS AND DISCUSSION

Z-Direction Variation of Internal Stress

The equivalence of internal and drying stresses, as discussed above, means in principle that it should be possible to measure the variation of drying stress in the z-direction by measuring the z-direction variation of internal stress, an idea proposed by Wiley (12).

To explore this possibility commercial 42-lb/1000 ft^2 linerboard was used. Conditioned samples were characterized, and in-plane and out-of-plane moduli were measured ultrasonically (2,13). The results for the sixteen sheets are given in Table I. Samples for stress relaxation measurements consisting of the whole board, wire, middle or felt sections were produced by surface grinding using a technique developed by Wink (14,15). These samples were similarly characterized after surface grinding.

Table I. Characterization of commercial 42-lb linerboard (avg. 16 sheets).

Sample	Basis Weight, g/m^2	IPC Cal, (mm)	Density, g/cm^3	E_x, GPa	E_y, GPa	G_{xy}, GPa	E_z, GPa	R, (E_x/E_y)
Avg.	207.5	0.287	0.723	10.47	4.26	2.51	0.0459	2.47
S.D.	1.699	0.0038	0.139	0.308	0.306	0.064	0.00156	0.212
%CV*	0.82	1.35	1.92	2.94	7.18	2.53	3.40	8.58

*Where %CV = coefficient of variation; E_x, E_y, and G_{xy} are the in-plane machine direction Young's modulus, the in-plane cross machine direction Young's modulus, and in-plane shear modulus, respectively. E_z is the z-direction longitudinal modulus.

Internal stress determinations in the machine and cross machine directions for the whole board, using the stress relaxation procedure employed by Johansson and Kubat (10), are shown in Fig. 1. These authors argue that the slope F of the linear portion of the stress-log time curve should be a linear function of the applied initial stress σ_o. Furthermore, the intercept on the stress axis should be equal to the internal stress σ_i. Values of internal stress determined by linear regression analysis of the data shown in Fig. 1 are 7.72 Nm/g and 1.56 Nm/g for the machine and cross machine directions, respectively. Internal stress measurements similarly determined

and other properties for the whole sheet, felt, middle and wire sections are given in Table II.

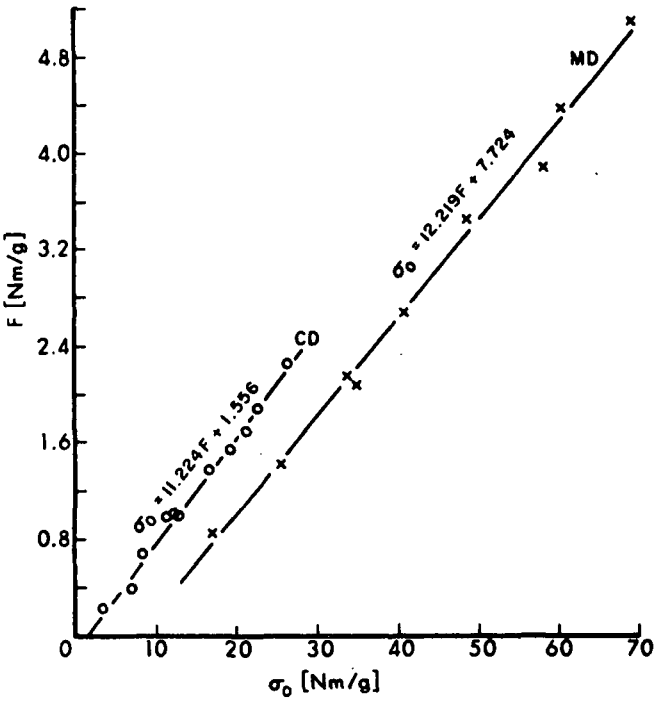


Fig. 1. Internal stress predictions from stress relaxation measurements.

There is indeed a significant variation in internal stress in the z-direction as seen in Table II. In the machine direction, the middle section has the lowest value of internal stress, while in the cross machine direction the wire side has the lowest value. The apparent density variation in the z-direction is not large. The out-of-plane longitudinal modulus is significantly lower in the middle section of the sheet, and a similar trend is found with the out-of-plane machine direction shear modulus. This behavior is similar to that reported by Waterhouse (4). It should be emphasized that, since these results are for a commercial linerboard, the interpretation is not unambiguous because of uncertainties with regard to composition, fines and fiber orientation distribution in the z-direction. The average properties of the felt, middle, and wire sections are generally less than those of the whole sheet. The question as to whether this may be due to damage from the surface grinding will be considered shortly. The stress relaxation method is viewed as an indirect method of determining internal stress and is rather time consuming. It would be of benefit to have a more direct measurement of internal stress to study its variation in the thickness direction.

When the various sections of the sheet were produced by surface grinding, a pronounced curvature development was observed. These are shown in Fig. 2. This curvature is a manifestation of the out-of-balance internal stress distribution which is created when the board is sectioned and is also direct evidence for the existence of internal stress variation in the z-direction.

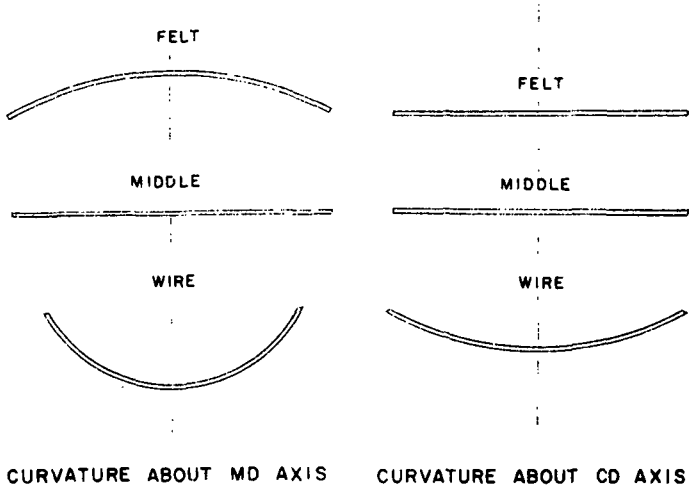


Fig. 2. Curvature measurements on 42-lb/1000 ft^2 linerboard sections.

Table II. Internal stress and other properties of 42-lb commercial linerboard.

Sample	Basis Weight, g/m^2	IPC Cal, mm	Density, g/cm^3	E_{MD}/ρ (km/sec)^2	E_{CD}/ρ (km/sec)^2	R	E_z/ρ (km/sec)^2	G_{xz}/ρ (km/sec)^2	G_{yz}/ρ (km/sec)^2	σi_{MD} Nm/g	σi_{CD} Nm/g
Felt side	94.1	0.1219	0.772	12.4	5.19	2.39	0.069	0.069	0.066	6.65	2.06
Middle	98.7	0.1358	0.727	11.4	5.04	2.27	0.043	0.068	0.066	3.95	3.12
Wire side	86.9	0.1191	0.729	12.1	3.81	3.17	0.059	0.077	0.068	5.61	1.10
Whole sheet	207.5	0.2870	0.723	13.1	6.23	2.10	0.064	0.106	0.086	7.72	1.56

Where G_{xz}/ρ and G_{yz}/ρ are the out-of-plane specific shear moduli and σi_{MD} and σi_{CD} are the specific machine and cross machine direction internal stresses.

A method for calculating the internal stress distribution, using curvature measurements has been developed. It is similar to that of Rybicki et al. (16), who used sectioning methods and strain measurements to calculate residual stress distributions in pipes and plates. The details are presented in Appendix A.

Radius of curvature, ultrasonic moduli, and calipers for the commercial linerboard sample are given in Table III.

Table III. Measurements for internal stress calculations.

Sample	Apparent Density, g/cm	Radius of Curvature, R cm	t mm	E/ρ $(km/sec)^2$
Felt side, MD	0.772	67.1	0.122	12.4
Felt side CD	0.772	8.08	0.122	5.19
Middle, MD	0.727	142.2	0.136	11.4
Middle, CD	0.727	28.2	0.136	5.04
Wire side, MD	0.729	8.46	0.120	12.1
Wire side, CD	0.729	3.68	0.120	3.81

Using this data and the equations given in Appendix A, we calculated the internal stress distributions shown in Fig. 3.

It is interesting to note that the center layer in both the MD and CD samples of the sheet is in tension, while the outside layers are in compression. Thermally toughened glass and polymers exhibit a similar behavior where the internal stress distribution is approximately parabolic, with the outside layers in compression and the center in tension.

Curvature and stress relaxation methods demonstrate a variation of internal stress in the z-direction. A significant variation in in-plane and out-of-plane properties has also been found. The equivalence of these two methods for internal stress distribution determinations and their relationship to drying stress has yet to be determined. In a recent review, Isayev and Crouthamel (17) question the meaning of internal stress measurements made using the stress relaxation technique, and they believe the method is unsuitable for determining the distribution of internal stress. The layer removal technique, together with curvature measurements, is preferred by Isayev and Crouthamel (17) for determining the internal stress distribution in polymer slabs produced by injection molding.

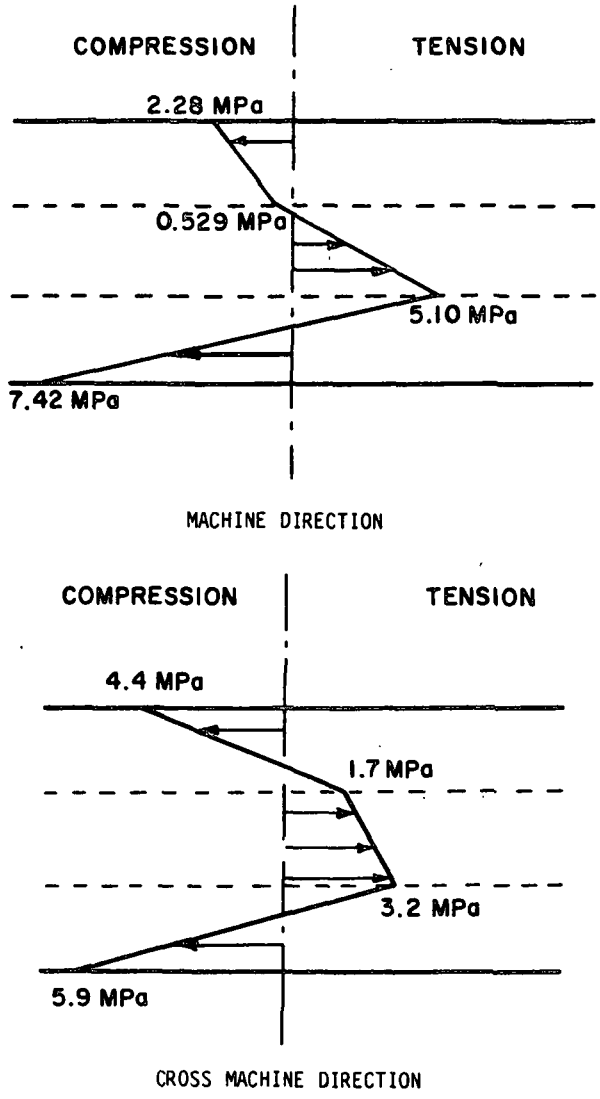


Fig. 3. Internal stress distrubtion for commercial 42-lb/1000 ft linerboard.

Let us give further consideration to Htun's (9) findings that the internal stress determined by stress relaxation is equivalent to the drying stress. When the drying process is completed, there is no resultant stress acting on the sheet (i.e., the drying stress has been reduced to zero), and therefore the average internal compressive stress, suitably computed, must be equal to the average internal tensile stress. Thus, it can be argued that the internal stress measured by Htun (9) should be equal to twice the average internal compressive (or tensile) stress measured using the curvature method.

A comparison of internal stress measurements made using stress relaxation (Table II) and curvature measurements (calculated from the stress distributions shown in Fig. 3) are given in Table IV.

Table IV. Comparison of internal stress measurements.

Direction	Stress Relaxation Method, Nm/g	Sectioning/ Curvature Method, Nm/g
MD	7.72	3.88 (2.29)
CD	1.56	3.09 (1.82)

The agreement, at least in magnitude, of the results by the two methods is encouraging, particularly in view of the assumptions made (see Appendix A) and the uncertainty in the interpretation of internal stresses as determined by the relaxation method. The calculations given in parentheses in Table IV are based on estimated values of elastic modulus for each of the sections at normal TAPPI testing conditions. In Instron tensile testing of the 42 lb/1000 ft^2 linerboard it had been found that $E_{Instron}/E_{Ultrasonic} \approx 0.59$. It is possible that the layer removal/curvature technique and analysis (which can account for the biaxial nature of the internal stress system) used by Isayev and Crouthamel (15) might yield more accurate results.

The internal stress variation determined using the stress relaxation method (Table II) implies, according to Htun, that the drying stress is higher in the surface layers than in the interior of the sheet. Modulus measurements tend to support this contention. There appears to be a contradiction, however, inasmuch as the internal stress distributions determined from layer removal and curvature measurements suggest the opposite effect; that is, the outside layers, which are ultimately in compression, should be subjected to a lower drying stress than the middle layer.

One possible resolution of this paradox is suggested. During the early stages of drying, the surface layers may experience a greater tensile drying stress than the interior. The phenomenon of stress reversal is common in glass and other polymer systems. During this phase, relaxation processes and stress activated molecular reorientation can occur more readily (18,19), thus yielding greater increases in moduli in the surface layers of the sheet, even though when dry these layers are in compression.

The variation of properties in the z-direction has also been measured on handsheets having a random fiber orientation and a high degree of uniformity. One set of handsheets was made on the Formette Dynamique and dried at 91°C for 30 min. Another set was made on an IPC handsheet former and then press-dried with upper platen temperatures of 121°C, 177°C, and 232°C, respectively, and a lower platen temperature of 96°C. The press loading was 400 psi (2.76 MPa). Three handsheets were press-dried at each temperature level and, after characterization, were surface ground to produce top, middle, and bottom sections. Nondestructive characterization of the whole sheet and sections is given in Table V.

Table V. Characterization of Formette and press-dried handsheets. Unbleached southern pine, 600 CSF.

Sample	IPC Caliper, mm	Basis Weight, g/m^2	Apparent Density, g/cm^3	Specific Modulus E/ρ, km/sec	Specific Modulus E_z/ρ, km/sec
Formette					
F-1 Top	0.0789	66.2	0.839	8.49	0.211
F-3 Middle	0.1041	87.4	0.840	9.05	0.158
F-2 Bottom	0.0899	73.9	0.821	10.5	0.218
Whole Sheet	0.2922	230.9	0.790	9.65	0.334
Press Dried					
121°C					
Top	0.0948	104.3	1.100	8.97	0.284
Middle	0.1029	103.7	1.008	6.61	0.123
Bottom	0.0878	78.4	0.893	5.03	0.098
Whole	0.2138	214.9	1.022	8.71	0.418
177°C					
Top	0.0972	107.1	1.101	9.54	0.281
Middle	0.1045	108.1	1.034	6.46	0.124
Bottom	0.0887	77.1	0.870	5.28	0.0919
Whole	0.2162	214.4	0.992	9.94	0.413
232°C					
Top	0.0983	106.6	1.084	9.09	0.253
Middle	0.1068	108.6	1.017	7.3	0.138
Bottom	0.0896	77.2	0.862	5.24	0.0829
Whole	0.2164	212.8	0.967	10.2	0.410

The results show significant property changes in the thickness direction, particularly for the press-dried handsheets. The higher density of the Formette handsheet sections when compared with the whole sheet is due to a reduction in roughness with surface grinding; however, the differences in density of the sections is not significant. The bottom or low temperature sections of the press-dried handsheets have a significantly lower density than the top and middle sections. This is in part responsible for the lower values of in-plane and out-of-plane moduli, the latter showing the greatest change. It is not known whether the overall reduction in out-of-plane modulus is due to the effects of surface grinding or to a change in internal stress distribution. It is clear, however, that significant gradients in properties can be induced by the large temperature gradients experienced by the press-dried handsheets. The effects of possible damage induced by surface grinding will now be briefly examined.

Samples of 42-lb/1000 ft^2 commercial linerboard were subjected to three levels of grinding, with 0.089, 0.044 and 0.013 mm of material being removed per pass to produce felt, middle and wire sections. Properties of these sections and the whole sheet are given in Table VI. If the properties are graphed as a function of the amount of material removed by grinding, no clear-cut trends are indicated. Some properties increase and some decrease as the severity of cutting is reduced. Nevertheless, an attempt was made to extrapolate the various properties to zero mm removed/pass, and the results are summarized in Table VII. The extrapolated values again indicate that there is a significant variation of elastic properties in the z-direction, particularly the out-of-plane properties. The variation in radius of curvature is also indicative of a significant variation in internal stress.

Isayev and Crouthamel (17) also investigated the effects of machining and found significant differences with the type of milling machine employed. They were also able to demonstrate, using annealed samples, that no significant curvature was induced with the method of choice.

Table VI. Effects of surface grinding treatment on section properties.

	mm removed/ pass	Apparent Density, g/cm^3	V_{MD}^2 $(km/sec)^2$	V_z^2 $(km/sec)^2$	Caliper, mm	Radius of Curvature, cm
Felt	0.089	0.719	12.98	0.0499	0.1051	4.51
	0.044	0.716	12.64	0.0511	0.1184	5.31
	0.013	0.728	12.39	0.0545	0.1118	5.40
Middle	0.089	0.705	11.48	0.0328	0.1150	14.0
	0.044	0.688	11.63	0.0311	0.1029	19.8
	0.013	0.701	11.75	0.0340	0.1187	8.6
Wire	0.089	0.656	11.10	0.0452	0.1053	3.09
	0.044	0.665	11.89	0.0434	0.1102	2.95
	0.013	0.657	12.08	0.0503	0.1045	2.82
Whole sheet	--	0.689	12.64	0.0571	--	--

Table VII. Extrapolated properties of surface ground sections.

	Apparent* Density g/cm^3	V_{MD}^2 $(km/sec)^2$	V_z^2 $(km/sec)^2$	R_{cm}
Felt	0.721	12.3	0.0555	5.45
Middle	0.698	11.8	0.0350	14.1
Wire	0.659	12.2	0.0530	2.80
Whole Sheet	0.689	12.6	0.0571	--

*Average values.

CONCLUSIONS

The variation of properties in the thickness or z-direction of paper and their relationship to papermaking process variables have been reviewed. Special attention has been given to the drying process and its effect on drying and internal stresses. It is argued that a paper, having a high degree of uniformity in the thickness direction, i.e., fiber orientation and bonding, can still have, due to its viscoelastic nature, a significant drying and internal stress variation in the z-direction.

Two methods have been used to measure the variation of internal stress, and both involve measurements on felt side, middle, and wire side sections of paper produced by surface grinding. The first method involves stress relaxation measurements, while the second involves curvature measurements. A significant variation of internal stress and physical properties in the z-direction has been measured on samples of commercial linerboard, Formette handsheets dried at 91°C, and press dried handsheets dried at temperatures of 121°C, 177°C, and 232°C.

In an attempt to compare the two methods, we found an order of magnitude agreement for the internal stress on the commercial linerboard sample.

When we examined the severity of surface grinding on section properties, no common trend was found; however, it is recommended that, although time consuming, the minimum amount of material removed/pass should not exceed 0.013 mm.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Betty John in making the Formette handsheets, Chris Devlin, an Institute graduate student, in making the press-dried handsheets, and Sheila Burton and the Editorial Staff in preparing the manuscript.

REFERENCES

1. Baum, G. A. "The Elastic Properties of Paper". Progress in Paper Physics Seminar. STFI Stockholm, Sweden, June 25-29 1984, to be published.
2. Habeger, C. "Measuring Z-direction elastic properties in paper with ultrasonic techniques". Progress in Paper Physics Seminar. STFI Stockholm, Sweden, June 25-29 1984, to be published.
3. Baum, G. A. Paper 19:65-67(1984).
4. Waterhouse, J. F. Tappi 67(6):104-108(1984).
5. Parker, J., Mih, W. C. Tappi 47(5):254(1964).
6. Kallmes, O. J. Tappi 52(3):482(1969).
7. Wickes, L. Tappi 65(9):124(1984)
8. MacGregor, M. A. Tappi 66(6):53(1983).
9. Htun, M. "The Influence of drying time and temperature on drying stress and related mechanical properties of paper". Doctoral Dissertation. Stockholm, Sweden, The Royal Institute of Technology, 1981.
10. Johansson, F., Kubat, J. Svensk Papperstid. 20:822 (Oct. 31, 1964).
11. Lindroos, S., Waterhouse J. F. unpublished work.
12. Wiley, J. H. "An investigation of Drying Stress Variation through the thickness of Paper". Student A-200 problem 399A, IPC June 16, 1982.
13. Baum, G. A. IPC Technical Paper Series Number 119, Dec. 1981.
14. Wink, W. A., Private Communication.
15. Beckman, N. J. and Plucker, E. I. TAPPI Coating Conference Preprint April 30-May 2, 1973.
16. Rybicki, E. F., Shadley J. R., Shealy W. S. Experimental Mechanics 438, Dec. 1983.
17. Isayev, A. I., Crouthamel, D. L. Polymer-Plast Technol. Eng. 22(2):177-232(1984).
18. Htun, M. Tappi J. 67(9):124(Sept. 1984).
19. Htun, M. "The Influence of Drying Strategies on Paper Strength" Progress in Paper Physics Seminar, STFI Stockholm, Sweden, June 25-29, 1984.

APPENDIX A

A procedure for calculating the internal stress distribution of paper using curvature measurements is given below. It is similar to that of Rybicki et al. (16) who used sectioning and strain gage measurements to calculate residual stress distributions in pipes and plates.

The analysis is developed for a board in three sections but is not limited to this number. The following assumptions are made.

1. the stress distribution is linear in each section
2. only elastic behavior is considered
3. the analysis is one dimensional and the stress distributions in the machine and cross machine directions are treated independently of each other.

Notation for the three sections is shown in Fig. A-1. The stress σ on each section is resolved into a tensile and bending stress. After sectioning, the tensile stresses go to zero and the bending contribution results in curvature of the section. The equilibrium force F and moment M equations for the three sections 1, 2, and 3 are:

$$F_1 + F_2 + F_3 = 0. \quad (1)$$

$$M_1 + M_2 + M_3 + F_1(t_1/2 + t_2 + t_3) + F_2(t_2/2 + t_3) + F_3\, t_3/2 = 0 \quad (2)$$

For each section the resultant stress is given by the following pair of equations.

$$\sigma_{1a} = F_1/t_1 + \bar{\sigma}_{1a}$$
$$\sigma_{1b} = F_1/t_1 - \bar{\sigma}_{1b} \quad (3)$$

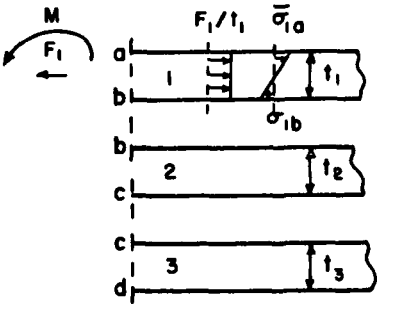


Fig. 1-A. Notation for internal stress analysis.

We also have the condition that

$$\bar{\sigma}_{1a} = \bar{\sigma}_{1b} = \bar{\sigma}_1 \tag{4}$$

and similarly for sections 2 and 3.

Stress continuity between sections also requires that

$$\sigma_{1b} = \sigma_{2b}$$

$$\sigma_{2c} = \sigma_{3c} \tag{5}$$

Using these conditions and equations (6) for the bending moment on each section, a set of equations for the determination of the unknown forces F_1, F_2, and F_3 can be derived. Knowing F_1, F_2 and F_3 the internal stresses can be calculated from equations (3) above.

$$M = \bar{\sigma}\, t^2/6 \tag{6}$$

$$F_1A + F_2B + F_3C + \sum_1^3 \bar{\sigma}\, t^2/6 = 0$$

$$F_1 + F_2 + F_3 = 0$$

$$F_1/t_1 - F_2/t_2 - (\bar{\sigma}_1 + \bar{\sigma}_2) = 0$$

$$F_2/t_2 - F_3/t_3 - (\bar{\sigma}_3 + \bar{\sigma}_2) = 0 \tag{7}$$

where the constants A, B, and C are:

$$A = t_1/2 + t_2 + t_3$$

$$B = t_2/2 + t_3$$

$$C = t_3/2 \tag{8}$$

Solution of these equations requires that the determinant.

$$\begin{vmatrix} A & B & C & \sum_1^2 \bar{\sigma} T^2/6 \\ 1 & 1 & 1 & 0 \\ 1/t_1 & -1/t_2 & 0 & -(\bar{\sigma}_1 + \bar{\sigma}_2) \\ 0 & 1/t_2 & -1/t_3 & -(\bar{\sigma}_3 + \bar{\sigma}_2) \end{vmatrix} = 0 \tag{9}$$

In using the equations $\bar{\sigma}_1$ and $\bar{\sigma}_3$ are calculated using curvature measurements and the following equation

$$\bar{\sigma} = Et/2R \tag{10}$$

where E is the elastic modulus, t the section thickness and R the radius curvature. Thus $\bar{\sigma}_2$, can then be calculated from equation (9).

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3467

PROCESS, PROPERTIES, PRODUCT RELATIONSHIPS

October 22, 1985

PROJECT SUMMARY

PROJECT TITLE: PROCESS, PROPERTIES, PRODUCT RELATIONSHIPS

PROJECT STAFF: G. A. Baum/C. C. Habeger

PROGRAM GOAL:

Date: 9/10/85
Budget: $105,000
Period Ends: 6/30/86
Project No.: 3467

Develop relationships between the critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

To improve our capability of characterizing paper and board materials.

To relate measured parameters to end-use performance (especially in the case of Z-direction measurements).

To relate measured parameters to machine and process variables.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

1. The importance of wet pressing, refining, and yield on ZD elastic properties has been studied and a paper written for publication. The paper will be available at the April PAC meeting.

2. The effects of pulp mill and paper mill process variables on Poisson ratios and C_{12} have been re-examined. The mean of the Poisson ratios decreased with increasing density.

3. A microwave device for measuring the level of fiber orientation in a sheet has been constructed and is currently being tested.

4. The robotic or automatic device for measuring paper in-plane elastic properties has been improved in several ways. The sampling area has been relocated to be in the center portion of the specimen and software written to allow measurements of in-plane properties at various angular displacements from the MD (in 5° steps).

5. Equipment has been acquired to decrease the measurement time for the out-of-plane elastic property measurements. Work is underway to automate this system.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

1. Work is progressing to improve the out-of-plane measurements of elastic properties. New transducers have been designed, fabricated, and tested which are superior to previous designs. Equipment has been acquired to automate data acquisition and handling.

2. The robotic or automatic device for measuring in-plane elastic properties has been modified to provide a much more positive action in the turntable assembly. The unit continues to function satisfactorily.

3. An in-plane ultrasonic measurement system has been installed in a Blue-M oven in which the temperature and humidity can be controlled. An automatic balance is mounted on the top of the oven so that a sample may be weighed continuously as oven conditions change (except during ultrasonic measurements). This unit is currently being tested.

4. The microwave device for measuring fiber orientation in paper has been tested on a number of grades with good results. Comparisons with other methods of estimating fiber orientation are underway.

5. A simple three dimensional network model has been developed which appears to be useful in explaining some observed effects. Much additional work is needed in this area, however.

6. A paper entitled "Z-Direction Properties: The Effects of Yield and Refining" was presented at the recently held FRC Conference in Oxford, England. This is IPC Technical Paper No. 156, a copy of which is attached as Appendix I.

PROJECT TITLE: Process, Properties, Product Relationships

PROJECT STAFF: G. A. Baum

PRIMARY AREA OF INDUSTRY NEED: Properties related to end uses

PROGRAM AREA: Performance and Properties of Paper and Board

Date: 6/1/85
Budget: $105,000
Period Ends: 6/30/86
Project No: 3467
Approved by VP-R:

PROGRAM GOAL:

Develop relationships between the critical paper and board property parameters and how they are achieved in terms of raw material selection, principles of sheet design, and processing conditions.

PROJECT OBJECTIVE:

To improve our capability of characterizing paper and board materials.

To relate measured parameters to end-use performance (especially in the case of Z-direction measurements).

To relate measured parameters to machine and process variables.

PROJECT RATIONALE:

It is important to understand the relationships between end-use performance and properties in order to improve paper and board products or maintain performance within close tolerances while effectively utilizing available raw materials, minimizing energy requirements, and minimizing environmental impacts.

RESULTS TO DATE:

Ultrasonic techniques for measuring in-plane and out-of-plane elastic properties of paper have been developed. A caliper gage has been designed and constructed to allow simultaneous measurement of caliper and Z-direction ultrasonic measurements. This caliper gage has been found to be comparable or superior to other methods of accurately measuring caliper. The effects of fiber orientation, wet pressing, wet straining and drying restraints on the in-plane and out-of-plane properties of paper have been studied. The in-plane and out-of-plane elastic parameters have been related to end use tests and converting performance in a number of cases.

PLANNED ACTIVITY FOR THE PERIOD:

1. In-plane and out-of-plane elastic constants will be measured on a representative group of samples differing in composition and structure and in different ambient environments. These data will be compared with use-oriented test results, where possible. Particular attention will be given to the effects of yield and refining level on ZD properties.

2. Specific scattering coefficients will be measured in heavy board materials differing in composition and structure. These will be used to predict relative bonded area.

3. Work on automation of the ZD velocity measurements is scheduled. Improvements in the existing apparatus are anticipated.

4. The effort to establish relationships between properties and end-use performance will continue.

5. Completion of a new automated laboratory device for measuring in-plane parameters that will be operator "friendly and fool proof".

STUDENT RELATED RESEARCH:

M. Forbes, Ph.D.-1985; B. Pankonin, Ph.D.-1985; B. Berger, Ph.D.-1987; B. Berger, M.S.-1984; D. Waterman, M.S.-1986; W. Westervelt, M.S.-1986. Bernie Berger, M.S.-1985, Bernie Berger, Ph.D.-1988.

Status Report

PROCESS, PROPERTIES, PRODUCT RELATIONSHIPS

Project 3467

Z-Direction Transducer Development

The major weakness in our present Z-direction, time-of-flight velocity measurement technique arises from our use of highly resonant transducers. The shortest, 1 MHz wavetrain that can be passed through a paper sample is about six cycles. The sample selectively attenuates the higher frequency components of the wave-train. This makes the wavetrain disperse causing the apparent time-of-flight velocity of the front end of the wavetrain to be larger than the phase velocity at the carrier frequency. It is necessary to deal with front end of the pulse since multiple reflections in the sample and the transducer components make the received signal a combination of disturbances through many paths soon after the front end of the signal arrives. Our time-of-flight velocity is calculated from the time of arrival of the first peak in the pulse. The relative shape of the front end of the pulse (and the time-of-flight velocity) depends on the phase of the signal exciting the transducer. Even though our measured velocities are greater than the phase velocity and they depend on the exciting pulse, we have made meaningful comparisons between samples by standardizing the phase setting of the exciting pulse. Conceptually this same problem could occur in our in-plane measurements; however, in-plane work is done at lower frequencies where fiber scattering is not the dominant loss mechanism and attenuation is not so strong a function of frequency. The effect of exciting pulse phase variability on the in-plane stiffness measurements is about 1%, while the out-of-plane uncertainty can be around 30%.

The frequency dependent attenuation disperses the pulse, causing the front end to arrive early and the back end late. Measuring time-of-flight with

the front end leads to an overestimate of the velocity by a amount dependent on the attenuation characteristics of the sample. A straight forward calculation shows that the way around this is to use the arrival time of the entire pulse to calculate the velocity. However, this is impossible with highly resonant, ceramic transducers since multiple reflected signals arrive before the shortest pulse is finished. If broad banded transducers were available, a time-of-flight of the entire first pulse could be taken before secondary signals arrive. The time-of-flight measurement of the full signal would be performed with a digital cross-correlation scheme similar to one used in our automated in-plane instrument. Since the out-of-plane measurements are made at 1 MHz, a very high speed ($\geq$ 100 MHz) analog to digital convertor is necessary to input the pulse to a computer for cross correlation analysis. Thus to take the ambiguity out of the Z.D. measurements, it is necessary to procure a high speed A to D converter with a computer interface and to build broad-band Z-direction transducers.

We have purchased the high speed A to D converter in the form of a Hewlett-Packard model 1980A digital oscilloscope. It has a parallel I.E.E.E. interface and will be interfaced to an IBM PC. The task of writing interface software and modyifing the present Apple computer cross-correlation software to the IBM PC will begin in October.

After considerable trial and error a design for broad-banded Z.D. longitudinal transducers has been prototyped and tested. Construction of the final version is underway. The active element for the new transducers is a thin (110 μm) plastic, piezoelectric film made of polyvinylidene fluoride (PVDF). This has two advantages over the ceramic piezoelectrics we presently use: (1) it has a much lower mechanical impedance and couples energy more efficiently into the sample; (2) it has a lower quality factor making the construction of

broad-band transducers practical. However, it is less sensitive and it is difficult to achieve comparable signal to noise ratios.

To increase sensitivity, the transducers are made of a stack of four layers of metalized, PVDF film. The two ply outer layers are stacked in series, while the two double layers are in parallel. The stack is held together with conductive epoxy. The outer surfaces are grounded and the center of the stack is the active electrode. The transducer backing is made of extruded (non-polarized) PVDF. This gives an excellent impedance match, eliminating back side transducer reflections. A layer of polystrene (for impedance matching) and a soft rubber disk (for coupling sound into the sample) compose the front end of the transducer. The result is that a pulse of a single cycle at 2 MHz can be transmitted through the sample with only a 50% loss in sensitivity compared to the ceramic transducers.

Mircowave Fiber Orientation Anisotropy Gage

The microwave fiber orientation gage, which was constructed last period, has undergone evaluation and some refinement in data gathering technique. We found that consistent, reproduceable results can always be obtained if the waveguide attenuator is maintained at (or above) 10 dB. We investigated the sensitivity of MD to CD signal transmission ratios to changes in fiber species, moisture content, and density. The results were relatively insensitive to the fiber changes, but the ratio climbed significantly, with increasing moisture and decreasing density levels. We can explain, in terms of basic theory, the sensitivity to moisture and density.

This technique is potentially non-destructive and applicable to on-line testing. It is the only existing fiber orientation measurement which could be

used on heavy grades on-line. A report on the microwave orientation instrument is currently being written.

Appendix I

IPC Technical Paper Series

Number 156

Z-DIRECTION PROPERTIES: THE EFFECTS OF YIELD AND REFINING

B. F. Berger and G. A. Baum
The Institute of Paper Chemistry
Appleton, Wisconsin, U.S.A.

ABSTRACT

The z-direction (ZD) elastic properties of paper have received little attention in the past because of measurement difficulties. This paper describes the effects of wet pressing, refining, and yield on three ZD elastic properties, C_{33}, C_{44}, and C_{55}. The elastic parameters were measured using ultrasonic methods on an unbleached kraft oak pulp. The ZD elastic parameters were very sensitive to wet pressing pressure. Increasing the level of refining or decreasing pulp yield produced increases in C_{33}, C_{44}, or C_{55}, which were greater than would be expected by wet pressing alone to the same density. A plausible explanation for this behavior is that the refining and yield changes also significantly change the ZD stiffness and shear stiffness of the fiber cell wall.

INTRODUCTION

The z-direction or thickness direction mechanical properties of paper have received much less attention than the in-plane properties because of the difficulty in measuring out-of-plane properties. Traditional measurements of elastic or strength properties of paper require that clamps or rigid platens be attached to the test specimen. In the thickness direction this usually means that adhesives must be used (except in compression) with the attendant adhesive penetration problems.

Wave propagation techniques can be used to measure the elastic properties of materials without requiring the use of adhesives. Such techniques have been adapted to paper (1-6). Because these measurements are non-destructive, it is possible to determine seven of the nine elastic parameters of paper (6) on a single specimen. This has led to a much better understanding of how machine and process variables separately and collectively affect the three-dimensional elastic response of paper. Some of the out-of-plane properties are far more

sensitive to certain process variables than are the corresponding in-plane properties. In addition, the research to date suggests that in many instances end use performance may be closely related to the (some times undetected) changes occurring in the z-direction during paper manufacture. Accordingly, the measurement of z-direction elastic properties should lead to an improved understanding of the manufacturing process and how it, in turn, relates to end use performance.

This paper briefly reviews some fundamentals and earlier work concerned with the effects of fiber orientation, wet pressing, and wet straining or drying restraints on paper z-direction elastic and strength properties, and then goes on to describe new results obtained for the effects of yield and refining.

BACKGROUND

Paper can be considered an orthotropic elastic material (2,3,6,7,8). An orthotropic material is one which has three mutually perpendicular planes of symmetry. For such a material the stresses, τ_{ij}, can be expressed in terms of the strains, ϵ_{ij} by

$$\begin{aligned}
\tau_{11} &= C_{11}\epsilon_{11} + C_{12}\epsilon_{22} + C_{13}\epsilon_{33} \\
\tau_{22} &= C_{12}\epsilon_{11} + C_{22}\epsilon_{22} + C_{23}\epsilon_{33} \\
\tau_{33} &= C_{13}\epsilon_{11} + C_{23}\epsilon_{22} + C_{33}\epsilon_{33} \\
\tau_{23} &= 2C_{44}\epsilon_{23} \\
\tau_{13} &= 2C_{55}\epsilon_{13} \\
\tau_{12} &= 2C_{66}\epsilon_{12}
\end{aligned}$$

The nine C_{ij} are called the elastic stiffnesses and have units of stress (Pa). Alternatively the nine stiffnesses can be written in terms of elastic compliances, S_{ij}, where $[S_{ij}][C_{ij}]=I$, or as engineering elastic constants. The latter include three Young's moduli, three shear moduli, and three Poisson ratios. While the elastic behavior of paper can be expressed in any of these three forms, the elastic stiffnesses are preferred since these may be measured directly using sound wave propagation techniques (6-9). Such techniques are valid as long as the wavelength of the sound wave is long compared to the characteristic dimensions of the fibers. In such cases the paper may be considered a homogeneous continuum.

The elastic stiffnesses C_{11}, C_{22}, C_{12}, and C_{66} are referred to as in-plane parameters since they are all defined in the MD-CD (or x-y or 1-2) plane. The elastic stiffnesses C_{33}, C_{44}, C_{55}, C_{13}, C_{23} are referred to as out-of-plane elastic parameters because they all involve the z-direction. It is this last group of "constants" (especially the first three) that is of interest to us in this paper. As will be discussed below, however, these quantities are not "constant" at all but are very sensitive to process conditions.

The appendix gives a brief description of how the engineering elastic constants are defined.

Previous work (for example, references 9-11) has shown that the in-plane and out-of-plane elastic properties of paper are very sensitive to paper machine process variables. It is well known, for example, that changes in rush-drag ratios (fiber orientation), wet pressing, or wet straining affect the in-plane Young's moduli. Less well understood is the affect of these and other variables on the out-of-plane elastic properties. Fleischman et al. (11) reported that C_{33} (related to E_{ZD}) was not sensitive to changes in fiber orientation (in the plane of the paper), but was extremely sensitive to wet pressing pressure and wet straining (wet draw) or drying restraints. Increased wet pressing pressure causes significant increases (up to tenfold) in ZD stiffness, C_{33}, and the out-of-plane shear stiffnesses. Fleischman's work also showed that the in-plane and out-of-plane elastic properties (and by implication other mechanical properties as well) are highly interrelated. That is, a change in a machine operating variable causes simultaneous changes in both in-plane and out-of-plane properties in quite predictable ways.

This is evident in the relationship that exists in paper between the shear modulus, G_{xy}, and the geometric mean of the in-plane Young's moduli (12), viz. $G_{xy} = a(E_x E_y)^{1/2}$. This expression was first deduced from considerations based on an isotropic material, for which $G = E/[2(1 + \nu)]$. This relationship also seems to hold for a number of orthotropic materials if the anisotropy is not too large and if E and ν are replaced by the geometric means (or some other suitable average) of the measured orthotropic parameters. Thus for the MD-CD plane in paper, perhaps it is not surprising that the

simple relationship holds for many (if not all) grades of paper manufactured on a Fourdrinier machine, since for these papers the anisotropy is usually less than three or so.

In reference 12 the value of a in the above expression was determined from measurements of the in-plane Poisson ratios to be 0.387 ∓ 0.007 (since $a^{-1} = 2(1 + (\nu_{xy}\nu_{yx})^{1/2})$. This value has since been confirmed for a large number of experimental and commercial papers in a number of laboratories. It appears to be quite insensitive to the method of paper manufacture or paper machine variables. Surprisingly, similar relationships have been found for the other two symmetry planes in the paper, even though the anisotropy in these planes is large. Specifically, for Fleischman's data (13), $C_{44} = 0.31(C_{22}C_{33})^{1/2}$ and $C_{55} = 0.25(C_{11}C_{33})^{1/2}$. The two coefficients in this case are determined from simple regressions, not from Poisson ratios, since the out-of-plane Poisson ratios are difficult to measure. The implication, however, is that shear in a given plane is related to the principal moduli in that plane.

If the three equations above are multiplied (14), one obtains $C_{11}C_{22}C_{33} = K_1C_{44}C_{55}C_{66} + K_2$. The value of K_1 would be the inverse product of the three coefficients in the three separate relationships and K_2 would be expected to be zero. This relationship, again using Fleischman's data representing samples that had different levels of fiber orientation, wet straining, and wet pressing but essentially constant basis weights, is plotted in Fig. 1. The slope of the regression line in Fig. 1 is about 41 with an intercept, K_2, not significantly different from zero. The densities resulting from the different processing conditions varied from about 0.4 to 1 gm/cm^3. A change in any one or more of the three variables defines a point along the straight line. It may be that some other process variables, which affect the properties of the fiber cell wall, might also change the slope of the line. Two such variables, yield and level of refining, have been studied and the results are presented and discussed in the following sections.

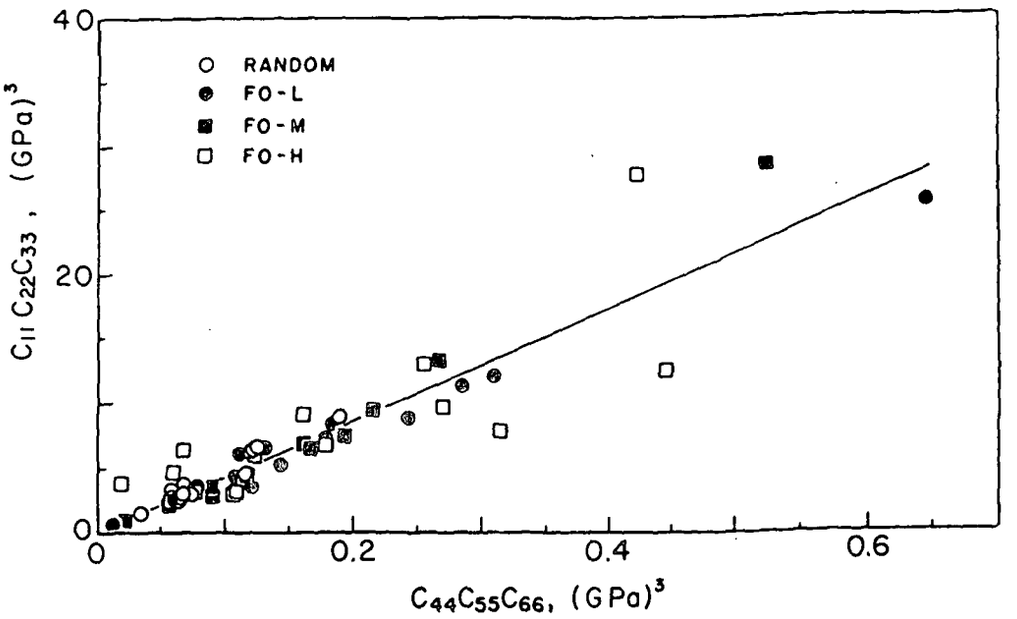


Figure 1. The product of the elastic axial stiffnesses vs. the product of the shear stiffnesses (Ref. 14).

THE EFFECTS OF YIELD AND REFINING ON ZD ELASTIC PROPERTIES

A red oak (Quercas rubra L.) was pulped to three yields using the kraft process by varying the cooking time and temperature (H-factor). Anisotropic sheets were prepared, using a Formette Dynamique, from each yield fraction using four refining levels in a Valley beater and four wet pressing pressures. The samples were dried under restraint in both the MD and CD. In addition, three levels of fiber orientation were used, but this work is not discussed here since the results are similar to those reported by Fleischman (11). Table 1 lists the various conditions studied.

The elastic stiffnesses for each sample were measured using ultrasonic wave propagation techniques (9). The calipers were determined using a soft rubber platen caliper gauge (15). Table 1 also presents six of the seven measured stiffnesses. (C_{12} is omitted from the table since it will not be discussed). Figure 2 shows C_{11} plotted against IPC (rubber platen) density. As expected, as the refining level is increased, the density at a given wet pressing level also increases, as does C_{11}. The

Table 1. Pulping and refining variables*.
(Last 3 digits of sample name are wet press pressure in psi.)

Name	IPC Density (g/cm^3)	Basis Weight (g/m^2)	Yield (2)	Kappa	Beat time (min)	CSF (ml)	FO (Arb.)	C_{11} (GPa)	C_{22} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{55} (GPa)	C_{66} (GPa)
1025	0.344	271	53.8	16.4	0	645	medium	4.36	2.13	0.0094	0.0193	0.0298	0.884
1050	0.431	270	53.8	16.4	0	645	"	6.1	2.94	0.0132	0.0286	0.0408	1.3
1100	0.576	270	53.8	16.4	0	645	"	8.68	4.31	0.0322	0.0524	0.0733	2.06
1250	0.582	271	53.8	16.4	0	645	"	8.5	4.03	0.0378	0.057	0.0791	1.93
2025	0.417	264	53.8	16.4	10	600	"	5.51	3.25	0.0218	0.0366	0.0517	1.3
2050	0.522	263	53.8	16.4	10	600	"	7.45	4.53	0.0344	0.0564	0.0773	1.84
2100	0.659	265	53.8	16.4	10	600	"	10	5.93	0.0729	0.0891	0.119	2.62
2250	0.658	266	53.8	16.4	10	600	"	9.93	5.87	0.075	0.0984	0.128	2.49
3025	0.658	274	53.8	16.4	35	330	"	10.4	6.1	0.137	0.14	0.172	2.84
3050	0.756	273	53.8	16.4	35	330	"	12.7	7.41	0.183	0.178	0.208	3.55
3100	0.865	275	53.8	16.4	35	330	"	14.1	9.32	0.298	0.212	0.242	4.1
3250	0.86	275	53.8	16.4	35	330	"	14.4	8.31	0.283	0.212	0.249	4.11
4025	0.733	263	53.8	16.4	50	170	"	12.9	7.36	0.223	0.186	0.215	3.53
4050	0.834	262	53.8	16.4	50	170	"	14.5	8.74	0.309	0.221	0.25	4.14
4100	0.955	273	53.8	16.4	50	170	"	16.1	9.73	0.447	0.248	0.285	4.73
4250	0.931	265	53.8	16.4	50	170	"	16.3	9.74	0.401	0.266	0.291	4.82
5025	0.593	265	56.5	31.7	35	450	"	8.82	5.06	0.0868	0.111	0.138	2.31
5050	0.696	263	56.5	31.7	35	450	"	10.7	6.97	0.129	0.143	0.172	2.93
5100	0.809	265	56.5	31.7	35	450	"	12.8	8.6	0.211	0.193	0.224	3.77
5250	0.812	268	56.5	31.7	35	450	"	12.7	8.47	0.207	0.173	0.207	3.66
6025	0.546	266	58.3	46.5	35	515	"	7.52	3.94	0.061	0.0775	0.105	1.92
6050	0.662	266	58.3	46.5	35	515	"	9.8	5.31	0.0977	0.107	0.141	2.54
6100	0.78	266	58.3	46.5	35	515	"	11.7	7.49	0.169	0.159	0.2	3.27
6250	0.778	269	58.3	46.5	35	515	"	11.5	6.77	0.172	0.151	0.195	3.17
7025	0.639	256	53.8	16.4	35	350	low	8.34	8.08	0.128	0.15	0.15	2.79
7050	0.736	260	53.8	16.4	35	350	"	9.79	9.24	0.178	0.18	0.18	3.37
7100	0.841	266	53.8	16.4	35	350	"	11.4	11.1	0.281	0.23	0.23	3.9
7250	0.827	267	53.8	16.4	35	350	"	12.1	10.4	0.266	0.207	0.207	3.89
8025	0.655	283	53.8	16.4	35	350	high	10.3	6.29	0.14	0.15	0.186	2.84
8050	0.755	286	53.8	16.4	35	350	"	12.8	7.35	0.198	0.175	0.217	3.47
8100	0.862	286	53.8	16.4	35	350	"	14.6	8.89	0.318	0.222	0.267	4.12
8250	0.845	286	53.8	16.4	35	350	"	14.4	8.88	0.289	0.217	0.259	4.12

*Red oak

effect of yield, in the narrow range studied, is not very great, although it can be seen that the higher yield samples tend to have a lower C_{11} stiffness at constant density. The out-of-plane properties, however, seem to be much more sensitive to yield and refining than the in-plane properties. Figure 3 plots C_{33} against density for the samples refined at different levels but at constant yield. The effects of refining and wet pressing on C_{33} are quite large; over the density range studied C_{33} increases by a factor of about 45. This is 4 or 5 times greater than the changes in C_{33} found by Fleischman (13) resulting from wet pressing over the same density range. At a constant density of 0.7 g/cm^3, for example, C_{33} increases by a factor of two due to the refining. The effect of increasing yield on C_{33} is shown in Fig. 4. At constant density, increasing yield causes a decrease in ZD stiffness. At a density of 0.7 g/cm^3 the decrease is about 40%. These results could be interpreted in terms of decreased interfiber bonding at the higher yield levels. The scattering coefficients were measured for some of the samples at a wavelength of 700 nm*. At densities near 0.7 g/m^3 the decrease in yield from 58.3 to 56.5% produced a decrease in scattering coefficient of about 5% and a decrease from 56.5 to 53.8% gave a 25% increase in scattering coefficient. Increased refining (0 to 50 minutes) decreased the scattering coefficient about 12% at the same density. From these results it appears that the observed 200% and 40% increases in Figs. 3 and 4, due to increased refining and decreased yield, respectively, cannot be explained by changes in interfiber bonding only. The results thus also suggest that decreased yield and increased refining lead to a stiffening of the cell wall in the dried sheet. Presumably this would represent increased intrafiber bonding in the cell wall.

Figures 5 and 6 show that C_{44} and C_{55}, respectively, vary with density and refining just like C_{33}. Increases in refining level on these two out-of-plane shear stiffnesses has a greater effect than just increasing density by wet pressing. The behavior with yield changes is also like that observed for the out-of-plane stiffness, as shown in Fig. 7 for C_{55}. The results for C_{44} are similar.

*The scattering coefficients of the heavy basis weight samples were measured at 700 nm in order to minimize scattering to get enough energy through the sheet to make the measurement. This should be permissible since the results are used in a comparative way.

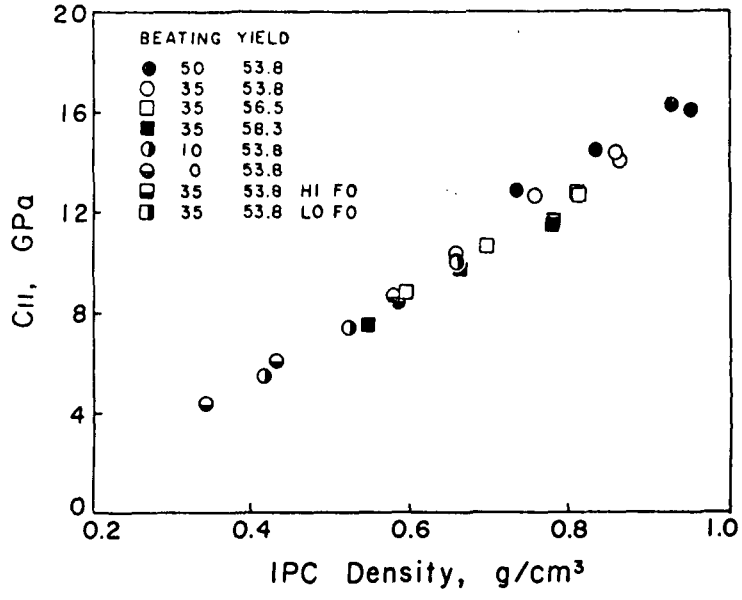


Figure 2. Elastic stiffness C_{11} vs. density at different refining and yield levels.

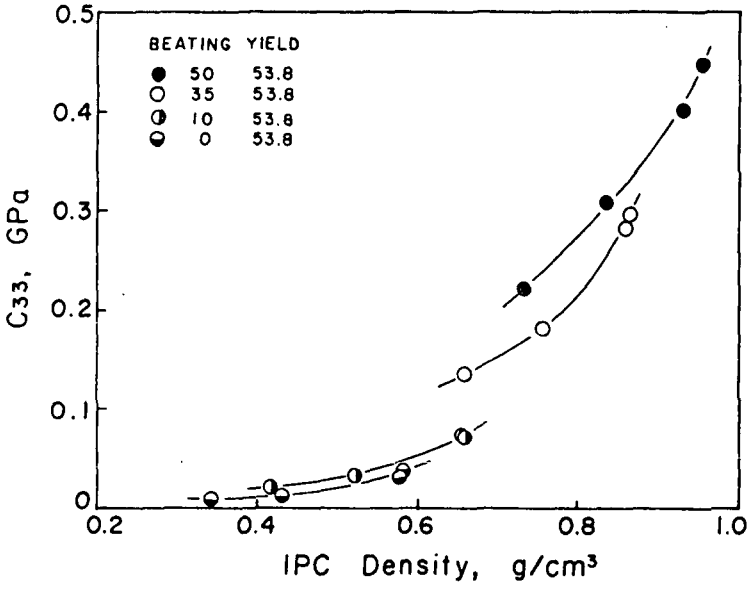


Figure 3. Elastic stiffness C_{33} vs. density at constant yield and four levels of refining.

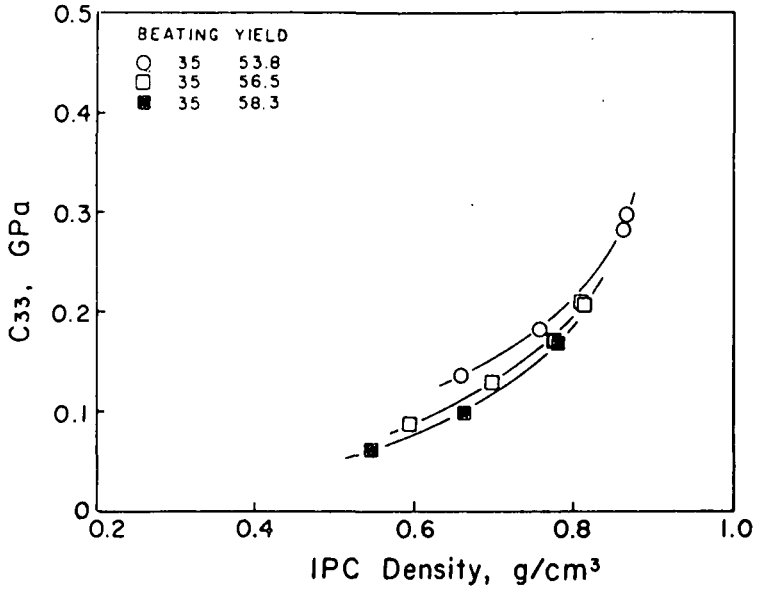


Figure 4. Elastic stiffness C_{33} vs. density at constant refining and three yield levels.

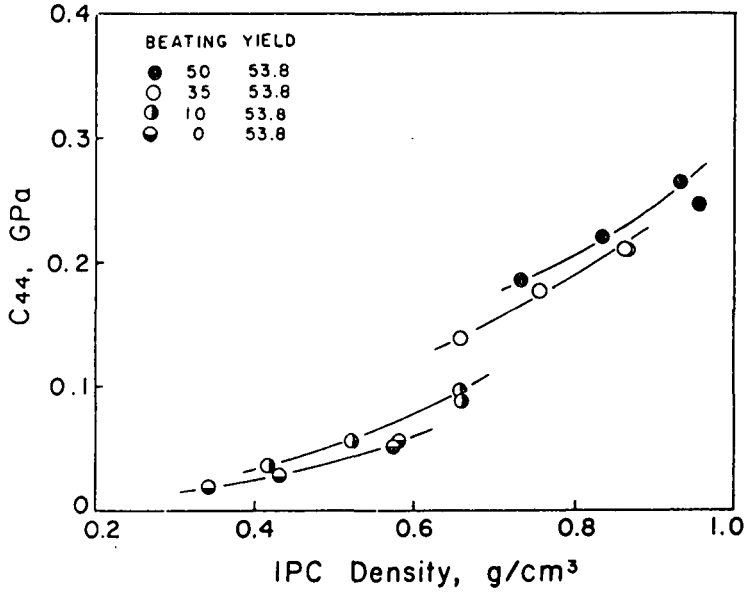


Figure 5. Elastic shear stiffness C_{44} vs. density at constant yield and four refining levels.

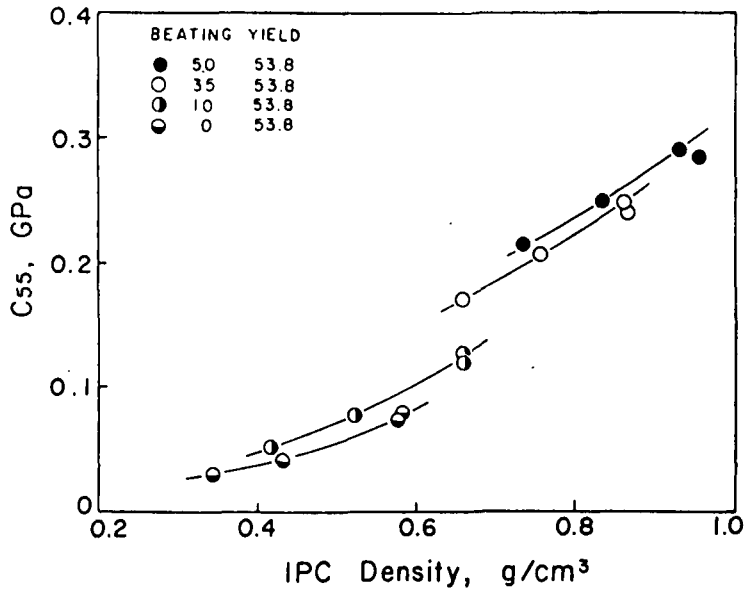


Figure 6. Elastic shear stiffness C_{55} vs. density at constant yield and four refining levels.

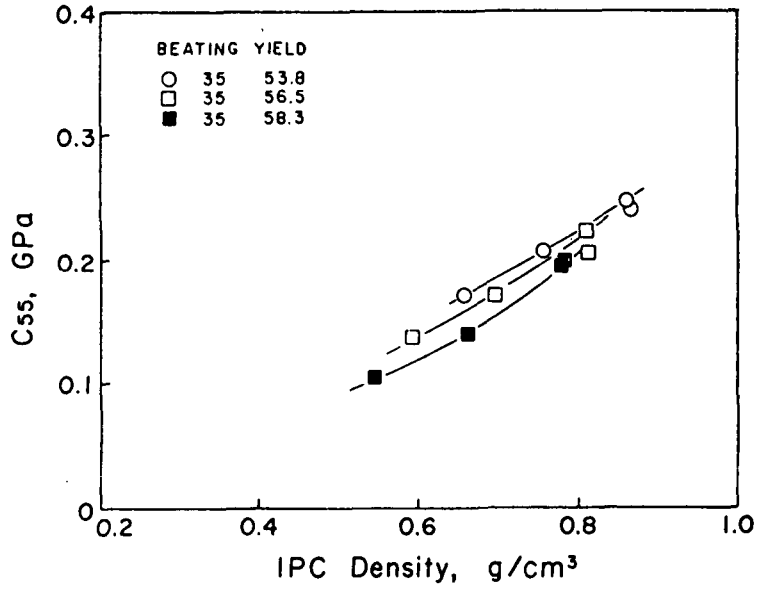


Figure 7. Elastic shear stiffness C_{55} at constant refining and three yield levels. The results for C_{44} are similar.

It appears that on a relative basis the ZD properties are much more sensitive to changes in yield or refining than the in-plane properties. If increased refining or decreased yield leads to a stiffer (less deformable) fiber cell wall in the transverse direction in the dried sheet, they would also increase the fiber cell wall shear stiffness. It would be difficult to separate the effects of increased interfiber bonding and increased intrafiber bonding, however, resulting from the changes in processing conditions.

The relationships between shear stiffness and the geometric mean of the two extensional stiffnesses in the same plane are shown in Fig. 8-10. Figure 8 is the situation for the MD-CD plane. The data form a nearly linear relation ship between C_{66} and $(C_{11}C_{22})^{1/2}$ with a slope of 0.397 $\mp$ 0.014. This slope should be compared with the previously mentioned value of 0.388. There does not, however, appear to be any major effects due to changes in yield or refining. Figures 9 and 10 show the relationships in the CD-ZD and MD-ZD planes, respectively. In both cases, a linear relationship exists at the lowest levels of the out-of-plane properties, but the data deviates from this behavior at the higher values. Note that in Figs. 8-10, the points which deviate from a simple linear relationship are those for the two highest refining levels and highest pressing pressures. In Fig. 8, for the MD-CD plane, the tendency seems to be toward slightly greater slope (points above the line) while in the CD-ZD plane (Fig. 9) and MD-ZD plane (Fig. 10) the data points fall beneath the line.

In some respects the results in Fig. 9 and 10 are surprising because the original argument which leads to a relationship between shear stiffness and the geometric mean of the in-plane Young's moduli assumes low anisotropy as discussed above. In the CD-ZD and MD-ZD planes in paper, however, the anisotropy ratios can easily be greater than 100 and are very sensitive to wet pressing and wet straining conditions (16). Hence, one could not anticipate relationships like those shown in Figs. 9 and 10.

In the earlier paper dealing with the relationship between shear and extensional stiffnesses in the MD-CD plane (12), it was observed that the relationship seems to hold until the anisotropy ratio R_{12} $(=C_{11}/C_{22})$ became greater than about 3.5. A

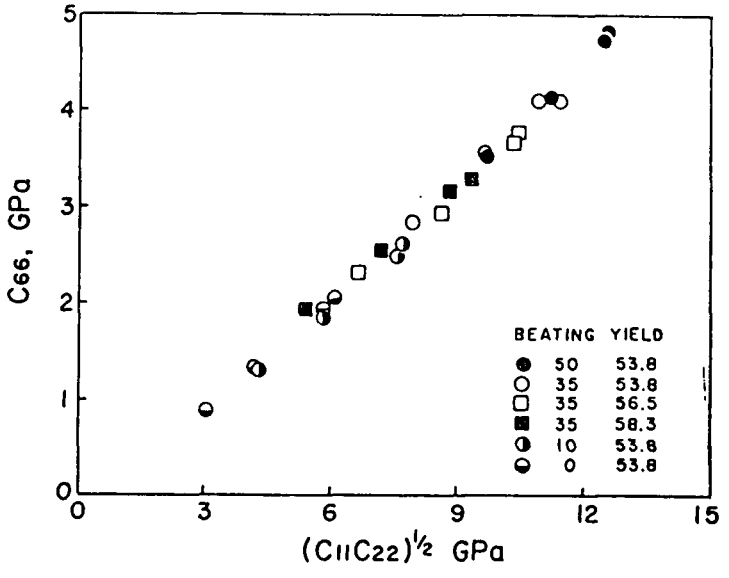


Figure 8. Elastic shear stiffness C_{66} plotted against the geometric mean of the in-plane elastic stiffnesses.

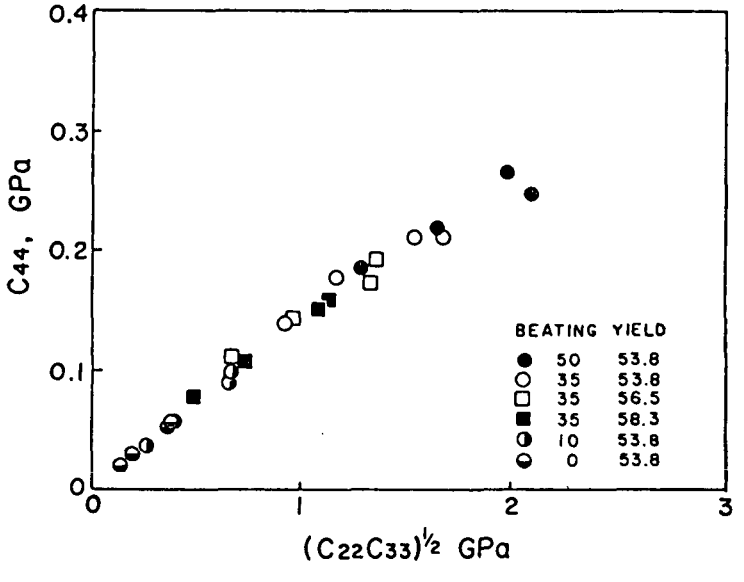


Figure 9. The elastic shear stiffness C_{44} plotted against the geometric mean of the elastic stiffness in the CD-ZD plane.

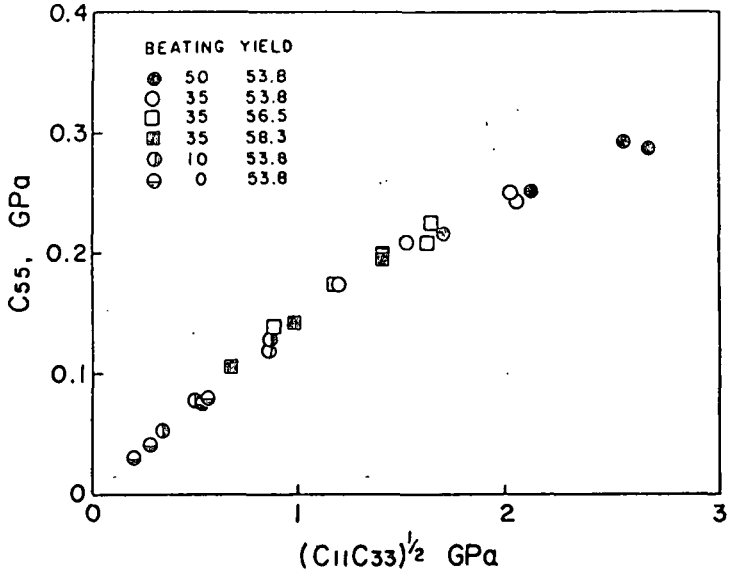


Figure 10. The elastic shear stiffness C_{55} plotted against the geometric mean of the elastic stiffnesses in the MD-ZD plane.

plot of the ratio of $C_{66}/(C_{11}C_{22})^{1/2}$ versus anisotropy for this study is shown in Fig. 11, but the range of R_{12} is so small that it is difficult to draw any conclusions concerning the coefficient. The results in Fig. 11 do imply, however, that one can expect greater anisotropy due to fiber orientation or/and drying restraint effects for unbeaten and/or high yield pulps. That is, the poorly bonded pulps in Fig. 11 seem to have greater values of R_{12}. The situation in the other two planes is depicted in Figs. 12 and 13. For either case the ratio is constant at the highest anisotropies, but decreases with decreasing anisotropy below about 60 in the CD-ZD plane and 110 in the MD-ZD plane. The significance of this is uncertain, but it would seem that the ratios should approach the in-plane value of 0.3 to 0.4 as the MD-ZD or CD-ZD anisotropies decreased toward lower numbers typical of the MD-CD plane. If so, a minimum must occur in the curves of Figs. 12 and 13 at an anisotropy between 1 and 25.

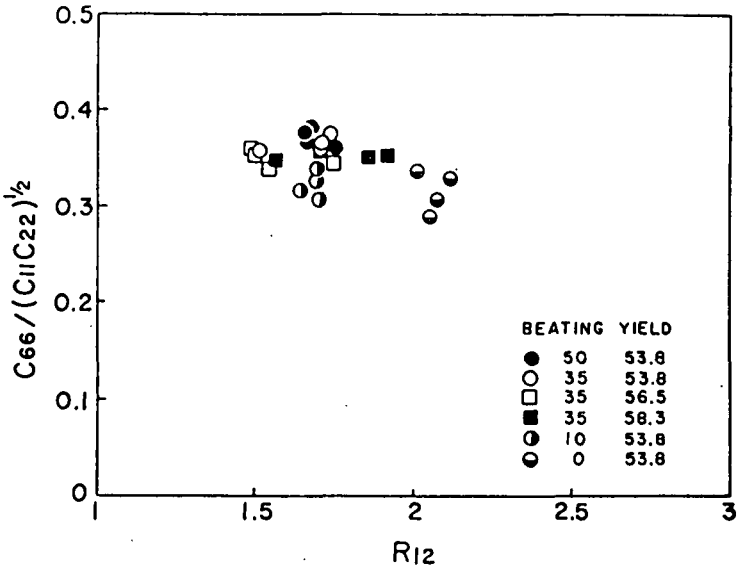


Figure 11. The ratio $C_{66}/(C_{11}C_{22})^{1/2}$ plotted against the anisotropy ratio $R_{12}(=C_{11}/C_{22})$.

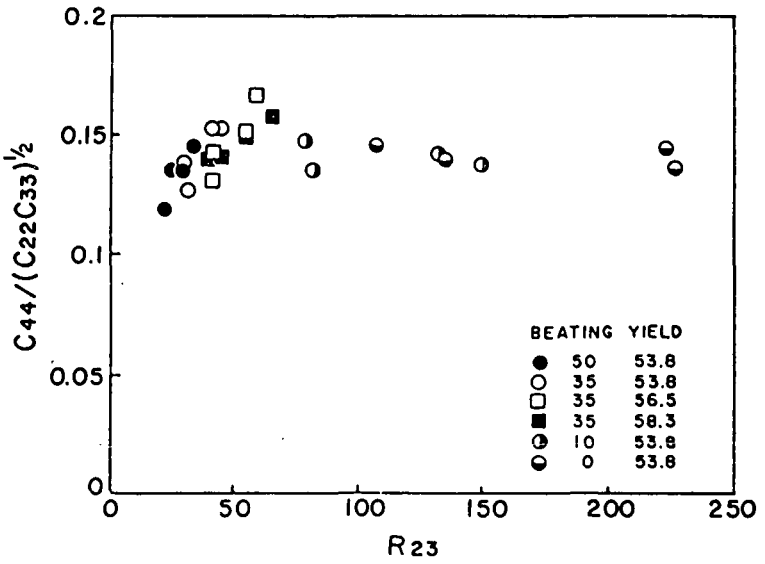


Figure 12. The ratio $C_{44}/(C_{22}C_{33})^{1/2}$ plotted against the anisotropy ratio in the CD-ZD plane $R_{23}(=C_{22}/C_{33})$.

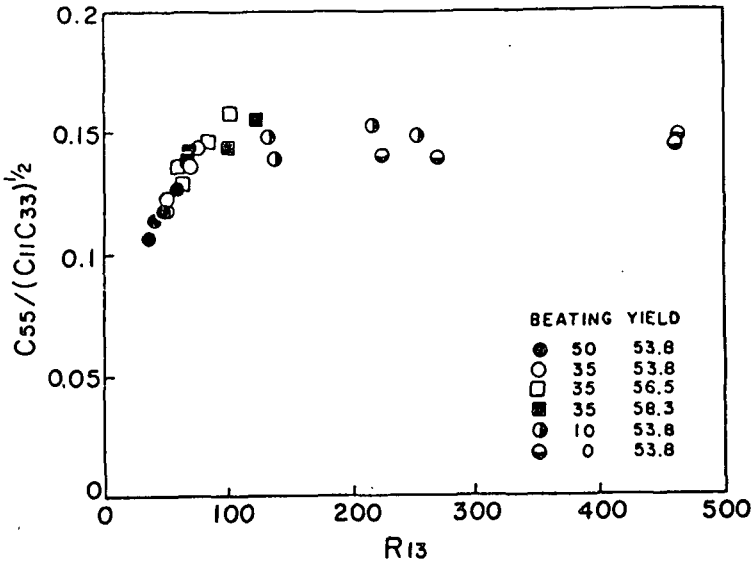


Figure 13. The ratio $C_{55}/(C_{11}C_{33})^{1/2}$ plotted against the anisotropy ratio in the MD-ZD plane $R_{13}(=C_{11}/C_{33})$.

The product of the three extensional stiffnesses plotted against the product of the three shear stiffnesses is shown in Fig. 14. There is a definite upward curvature in the data. The quantities plotted in Fig. 14 are interchanged from those in Figs. 8-10, so that the curvature in Fig. 14 is actually consistent with the trends shown in Figs. 9 and 10. Note also that two additional data sets are included in Fig. 14, representing two different levels of fiber orientation (random and high) at the lowest yield level and 35 minute refining level (see Table 1). These additional sets show that data resulting from changes in fiber orientation still fall along the curve. The curve is best fit with a power law relationship, $C_{11}C_{22}C_{33} = 161.1\ (C_{44}C_{55}C_{66})^{1.024}$, where R = 0.996. For Fleischman's data in Fig. 1 the power law relationship is $C_{11}C_{22}C_{33} = 47.3\ (C_{44}C_{55}C_{66})^{1.061}$ with R = 0.971.

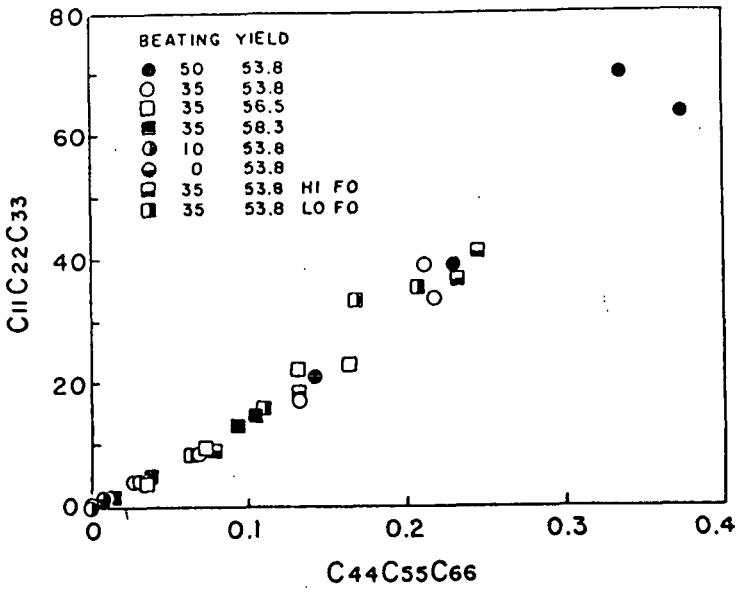


Figure 14. The product $C_{11}C_{22}C_{33}$ plotted against the product of the shear stiffnesses $C_{44}C_{55}C_{66}$. Compare to Fig. 1.

DISCUSSION AND CONCLUSIONS

The results shown in Figs. 3-7 clearly show the large effects in ZD properties caused by changes in yield, refining, and wet pressing. The changes with yield and refining are greater than would be expected from densification caused by wet pressing alone. Thus it appears that changes in the cell wall brought about by increased refining or decreased yield (lignin and hemicellulose removal) may directly impact the measured ZD properties of the paper. This would be consistent with the work of Seth and Page (17) who discovered that the stress-strain behavior of paper is directly related to the stress-strain behavior of the fiber cell wall for well bonded sheets. There should be quite a difference, of course, between straining a sheet in the ZD compared to the MD-CD plane.

Figure 15 attempts to illustrate these differences. The upper figure (a) depicts an unstrained cross-section of paper. Figure 15b shows the situation for a uniaxial strain in the MD

or CD. Some fibers are primarily strained along their axis (deformed in their width-axis (W-A) and thickness-axis (T-A) planes), while others experience only shear strains in their width-thickness (W-T) plane or axis-thickness (A-T) plane. Since the collapsed fibers tend to lie in the MD-CD plane, the interfiber bonds, are primarily stressed in a shear mode in the MD-CD plane. Figure 15c shows the case for ZD straining. Here the fibers predominantly experience transverse strains, but some deformation in the fiber W-A plane must also occur. The fiber-fiber bonds in this case are primarily strained in the ZD, in contrast to the situation in Fig. 15b. Figure 15d depicts shear in the MD-ZD or CD-ZD plane. This case would seem to be a sort of a combination of Figs. 15b and 15c, since all of the types of stresses must exist in most of in the fibers and bonds.

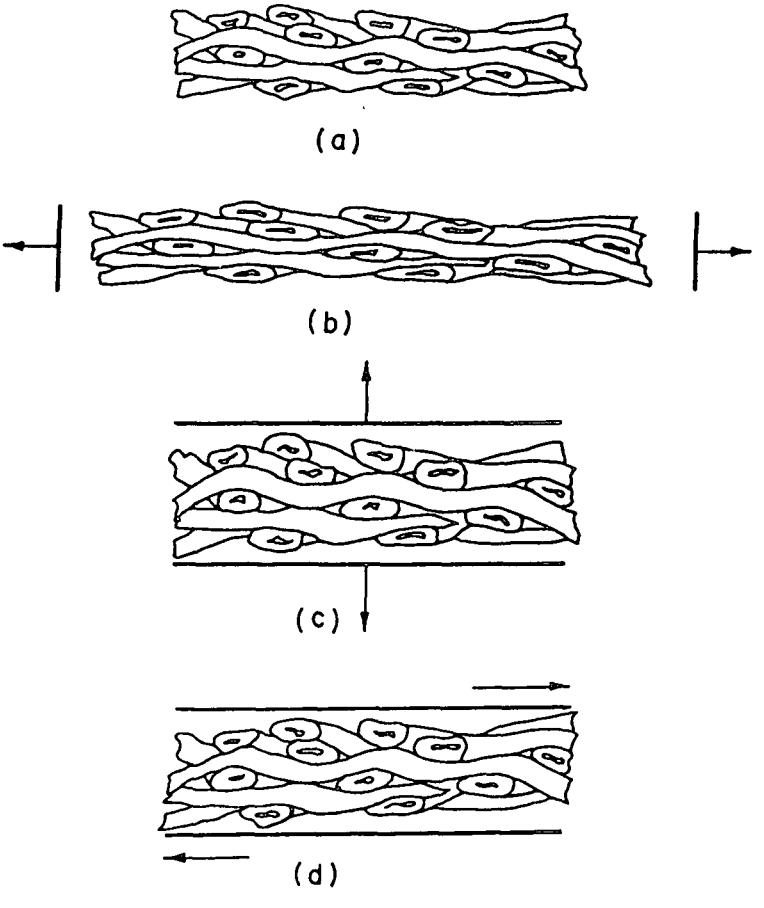


Figure 15. Modes of deformation in the MD-ZD or CD-ZD plane. (a) undeformed state; (b) MD or CD straining, (c) ZD straining, (d) shear strain in the MD-CD or CD-ZD plane.

The representation above with respect to the bonds probably is too simple, since the microcompressions resulting from drying must impart a three-dimensional character to the fiber-fiber bonds. This 3D character would likely produce a fiber-fiber bond shear strength (in the MD-CD plane) greater than that expected for two smooth surfaces bonded together and placed in shear. The same argument may apply in the case of ZD straining. It is known, for example, that wet straining or drying restraints dramatically reduce C_{33} or ZD tensile strength (ZDT). Since these process variables would also reduce the occurrence of microcompressions, perhaps it is the latter which contribute to the greater ZD stiffness and strength for unstrained sheets or sheets dried with no restraint. That is, perhaps microcompressions lead to greater ZD stiffnesses and strengths because of the three dimensional character they impart to the bond.

In the case of ZD properties, however, it should be realized that the transverse fiber properties are the ones that are important, as Fig. 15c and 15d above try to illustrate. Since most fibers in paper lie in the (MD-CD) plane of the paper, it is the ZD properties of the fibers themselves that influence the ZD sheet properties. There are two things to look at with respect to fiber ZD properties. First there is the question of lumen collapse, directly related to the conformability of the fiber which in turn is affected by the pulp yield and level of refining (among other things). The more refining and the lower the lignin content the more conformable the fiber becomes in the wet state and the greater the likelihood it collapses under "normal" pressing pressures or surface tension forces. Once the lumen has collapsed it must stay collapsed if high ZD stiffness (or strength) is required in the paper product. This means that (hydrogen) bonds must form across the collapsed lumen, otherwise it would open up under ZD loading and act as a low modulus region (18). One would expect lignin removal and internal fibrillation, caused by extensive beating, would contribute greatly to this ZD stiffness in the dried fiber.

The other factor which would contribute to fiber ZD properties is the presence or lack of the lignin and hemicellulose "matrix" in the secondary cell wall. A wood pulp fiber is an excellent example of a "fiber reinforced composite" in which

the fibrils in the cell wall are the "fiber" in the composite. The lignin and hemicelluloses are the matrix material of the composite. When the lignin is removed by pulping and the fibrils can bond to each other, (perhaps in conjunction with the hemicelluloses), a much more homogeneous and stiffer structure results in the dried fiber. This "stiffer" fiber in the ZD then leads to a stiffer and stronger paper in the ZD. The removal of both lignin and hemicellulose may produce a situation where "fibril to fibril" bonds cannot readily occur, thereby weakening the fiber cell wall. It has been shown that lignin and hemicellulose removal does decrease fiber-fiber bond strength (19). It would seem likely that without sufficient matrix material to distribute the loads between fibrils, the cell wall is more apt to fail in a brittle fracture mode during ZD straining.

While the above arguments concerning the effects of yield and refining on the ZD elastic properties of paper and fibers seem reasonable and agree with the data, they are, of course, only conjecture. Only a few studies have been carried out examining fiber ZD properties and the nature of fiber-fiber bonds strained in a normal (to the bond surface area) direction (e.g. Refs. 18 and 20). Perhaps this is an area which deserves more attention.

The results presented in Figs. 8 through 14, while not completely understood, have some practical applications. For example, since the shear modulus in any plane is related to the geometric mean of the Young's moduli in that plane, process variables like fiber orientation or wet straining, which change anisotropy do not affect the shear modulus if the anisotropy ratio is less than three or so. One might use the shear stiffness values when studying furnish changes or wet pressing changes since the shear values would be insensitive to other changes which might be occurring simultaneously (e.g. fiber orientation or wet straining). This scheme has already been used in the case of on-machine measurements to help separate changes in the furnish from changes in machine operating variables for the eventual purpose of papermachine control (21). For those who model containers or other structures, the simple relationships between shear and extensional stiffnesses can often make the model simpler or minimize the amount of data gathering (or guessing) necessary. A value for the in-plane

shear modulus, for example, which would be needed in most box or tube models is not easily measured, but can be estimated from the Young's moduli which can be easily measured.

The results suggest that in many cases fewer than nine elastic parameters will be required to obtain a good description of the mechanical response of paper and how it is impacted by changes in process variables. It is important to note, however, that one or more z-direction parameters must be included in the description. We believe that a more thorough look at z-direction properties, and how they are influenced by machine variables, will be a fruitful path to follow.

APPENDIX: ENGINEERING ELASTIC CONSTANTS

The meaning of the engineering elastic parameters can be understood by referring to Figs. 16 to 18. Figure 16 defines the three principal directions. The machine direction is referred to as MD (or x or 1), the cross direction as CD (or y or 2), and the thickness direction as ZD (or z or 3). If we apply a uniaxial stress to the sample in any one of these three directions we could deform the small element in one of the modes shown in Fig. 17. The ratio of the applied stress to the resultant strain (at small strains) is defined as the elastic modulus or Young's modulus in the direction of straining. The three modes of deformation shown thus result in three Young's moduli: E_{md}, E_{cd}, and E_{zd}. In addition, for any of the three modes shown in Fig. 17, the Poisson ratio would be defined as the ratio of the lateral contraction to the axial extension in the direction of straining. For the upper left hand figure, for example, two Poisson ratios could be defined since the specimen contracts in both the CD and ZD. These would be referred to as ν_{cd-md} and ν_{zd-md}, or ν_{yx} and ν_{zx}, respectively. The three modes of deformation shown in Fig. 17 thus yield six Poisson ratios, but only three of these are independent. These are normally taken to be ν_{xy}, ν_{xz}, and ν_{yz}. The elastic stiffnesses, C_{ii}, are related to the Young's moduli and Poisson ratios. For example $C_{11} = E_{md}/(1-\nu_{xy}\nu_{yx})$, etc. Figure 18 shows three modes of shear deformation, where the applied stresses are parallel to one of the principal directions. In these cases, a push or pull on opposite sides (or faces) of the specimen results in a shear deformation. The three independent shear stiffnesses shown correspond to each of the three planes of symmetry. The elastic parameters E_{md}, E_{cd}, G_{xy} (G_{md-cd}),

and ν_{xy} (ν_{md-cd}) are referred to as in-plane elastic constants because they are all defined in the MD-CD plane, whereas the parameters E_{zd}, G_{xz}, G_{yz}, ν_{xz}, and ν_{yz} are called out-of-plane elastic constants because they all involve the z-direction.

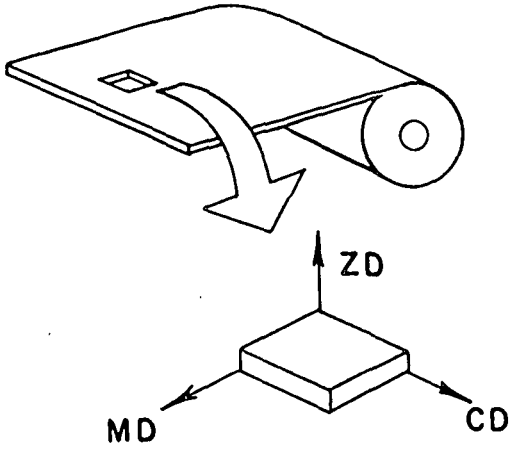


Figure 16. Principal directions assigned to paper.

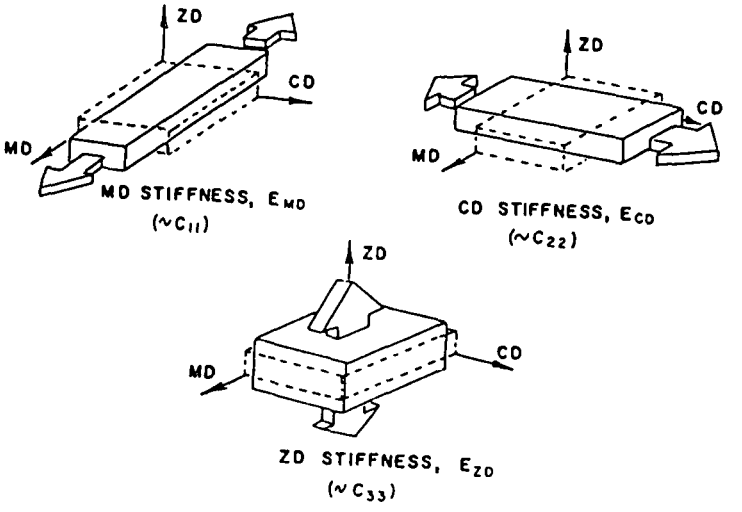


Figure 17. Three modes of deformation in uniaxial tension.

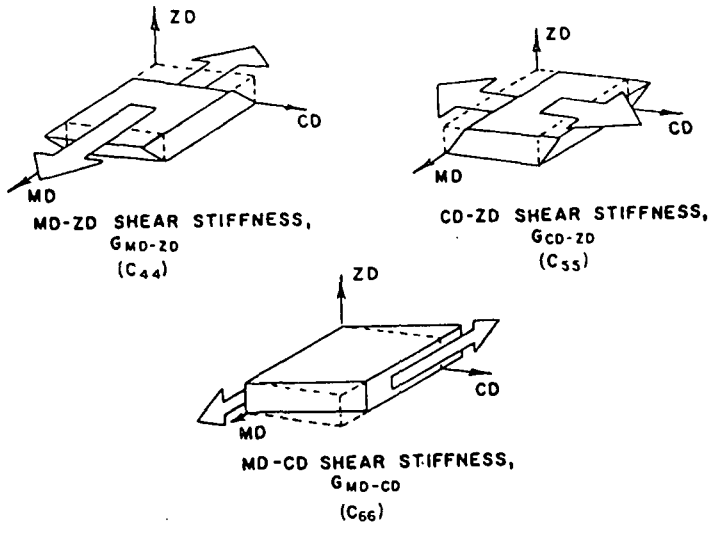


Figure 18. Three modes of deformation in shear.

ACKNOWLEDGEMENTS

The authors would like to express their thanks and appreciation to Messrs. C. Habeger, D. Wahren, J. Waterhouse, and W. Whitsitt, who read the manuscript and offered valuable comments and criticism, and to W. Shillcox who measured the scattering coefficients.

REFERENCES

1. Craver, J. K. and Taylor, D. L., Tappi 48 (3):142(1965).

2. Taylor, D. L. and Craver, J. K. Anisotropic elasticity of paper from sonic velocity measurements. In: F. Bolam's Consolidation of the Paper Web, Vol. 2, p. 852-72. London Tech. Section of the British Paper and Board Makers' Assoc., Inc. 1966.

3. Habeger, C. C., R. W. Mann, and G. A. Baum, Ultrasonics 17(2):57(1979).

4. Baum, G. A. and Bornhoeft, L. R., Tappi 62 (5):87(1979).

5. Mann, R. W., Baum, G. A., and Habeger, C. C., Tappi 62(8): 115(1979).

6. Mann, R. W., Baum, G. A., and Habeger, C. C., Tappi 63(2): 63(1980).

7. Jones, A. R., Tappi 51(5):203(1968).

8. Johnson, J. N., J. Appl. Phys. 42, 5522 (1971).

9. Baum, G. A., C. C. Habeger, and E. H. Fleischman, "Measurements of the Orthotropic Elastic Constants of Paper", in The Role of Fundamental Research in Paper Making, J. Brander, ed., Transactions of the Symposium held at Cambridge: September 1981. Mechanical Engineering Publications Ltd., London 1983.

10. Setterholm, V. and Kuenzi, E. W., Tappi 53 (10):1915(1970).

11. Fleischman, E. H., Baum, G. A., and Habeger, C. C., Tappi 65(10):115 (1982).

12. Baum, G. A., Brennan, D. G., and Habeger, C. C., Tappi 64 (8):97(1981).

13. Fleischman, E. H. Jr., "An Investigation of the Elastic and Dielectric Anisotropy of Paper", Ph.D. Thesis, The Institute of Paper Chemistry, Appleton, WI, June, 1981.

14. Baum, G. A. "The Elastic Properties of Paper: A Review" presented at the STFI/Tappi Progress in Paper Physics Seminar. Stockholm, 1984. To be published.

15. Wink, W. A. and G. A. Baum, Tappi 66(9):131(1983).

16. Baum, G. A., K. Pers, D. R. Shepard, and T. R. Ave'Lallment, Tappi J. 67(5):100(1984).

17. Seth, R. S., and D. H. Page, "The Stress Strain Curve of Paper" in The Role of Fundamental Research in Papermaking, J. Brander, ed., Transactions of the Symposium held at Cambridge, September, 1981, Mechanical Engineering Publications Ltd., London, 1983.

18. Hartler, N. and J. Nyren, "Influence of Pulp Type and Post-Treatments on the Compressive Force Required for Collapse in the Physics and Chemistry or Wood Pulp Fibers", Tappi STAP No. 8, Tappi Press, Atlanta, GA, 1970.

19. Hartler, N. and U-B Mohlin. Svensk Papperstidning 8: 295(1975).

20. Luce, J. E., "Transverse Collapse of Wood Pulp Fibers: Fiber Models" in The Chemistry and Physics of Wood Pulp Fibers, Tappi STAP No. 8, Tappi Press, Atlanta, GA, 1970.

21. Baum, G. A., and C. C. Habeger (to be published).

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3527

MEASUREMENT OF FIBER PROPERTIES AND FIBER-TO-FIBER BONDING

October 22, 1985

PROJECT SUMMARY

Date:	9/10/85
Budget:	$65,000
Period Ends:	6/30/86
Project No.:	3527

PROJECT TITLE: MEASUREMENT OF FIBER PROPERTIES AND FIBER-TO-FIBER BONDING

PROJECT STAFF: K. W. Hardacker, G. A. Baum

PROGRAM GOAL: Bring new attributes to wood-based products.

PROJECT OBJECTIVE:

The ultimate project objective is to define steps for making a paper of superior strength and with superior performance at high humidities. The immediate objective is to develop instrumentation to measure fiber mechanical properties in order to better understand the action of water in degrading fiber strength, stiffness, and fiber-fiber bonding.

PROJECT RATIONALE, PREVIOUS ACTIVITY, and PLANNED ACTIVITY FOR FISCAL 1984-85 are on the attached 1984-85 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

The instrument was assembled and underwent operation tests, debugging, and calibration.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

Fixtures and techniques are being developed for measuring the bond strength of fibers attached to the edges of microscope cover slips. This configuration is illustrated in the attached report. Also, a precision-ground differential lead screw has been ordered to replace the original cut-thread screw, which was found to have unacceptable pitch variations.

PROJECT TITLE: Measurement of Fiber Properties and Fiber-to-Fiber Bonding

PROJECT STAFF: K. W. Hardacker, G. A. Baum

PRIMARY AREA OF INDUSTRY NEED: Properties related to end uses

PROGRAM AREA: Moisture tolerant, superior strength paper and board.

Date: 6/1/85
Budget: $65,000
Period Ends: 6/30/86
Project No.: 3527
Approved by VP-R:

PROGRAM GOAL: Bring new attributes to wood-based products.

PROJECT OBJECTIVE:

The ultimate project objective is to define steps for making a paper of superior strength and with superior performance at high humidities. The immediate objective is to develop instrumentation to measure fiber mechanical properties in order to better understand the action of water in degrading fiber strength, stiffness, and fiber-fiber bonding.

PROJECT RATIONALE:

At present, commercial papers do not attain strength levels that realize the full potential of existing wood fibers. Most paper mechanical properties are markedly degraded with increasing paper moisture content. We need to better understand the nature of these changes in fiber properties and fiber-to-fiber bonding with increasing moisture content if we are eventually to improve the moisture tolerance of paper.

RESULTS TO DATE:

A literature search has been conducted. Ultrasonic techniques have been used to measure the in-plane and out-of-plane elastic constants of paper up to moisture contents of 60%. Above about 40% moisture, the water in the sheet dominates the measurement.

An instrument to measure axial or transverse fiber mechanical properties and fiber-fiber bond strength has been designed and constructed. It is currently being adjusted and calibrated.

PLANNED ACTIVITY FOR THE PERIOD:

The initial plans are to make measurements of fiber properties and fiber-to-fiber bonding as functions of moisture content, refining, yield, and pulping method. The measurements will include both axial and transverse properties. The initial work will be with softwoods.

POTENTIAL FUTURE ACTIVITIES:

Construction of the stated piece of equipment will lead to a number of applications in other research areas.

Status Report

MEASUREMENT OF FIBER PROPERTIES AND FIBER-FIBER BONDING

Project 3527

One facet of the development of moisture tolerant, superior strength paper is the determination of the effects of moisture on the individual fibers and on the bonds between the fibers. Measurements of the following properties are indicated:

1. Fiber axial tensile load/elongation characteristics
   - Breaking stress
   - Breaking strain
   - Work to rupture
   - Initial modulus
2. Tensile characteristics of various bonded-fiber-pair configurations.
3. Fiber transverse tensile load/deformation characteristics.
4. Fiber (and crossed fibers) transverse compression load/deformation characteristics.
5. Fiber cell wall shear modulus.

A literature survey was made to determine how other investigators had made these measurements. No single method appeared well suited to making all the desired measurements. In fact, the Institute's existing Fiber Load Elongation Recorder (FLER I), with suitable fixtures, could be used for measurements 1-4 except for marginal sensitivity for the transverse measurements.

Rather than try to upgrade the FLER I, it was decided to design and construct a versatile new instrument with adequate range and sensitivity.

This new instrument, the FLER II, has been assembled and is shown in Fig. 1.

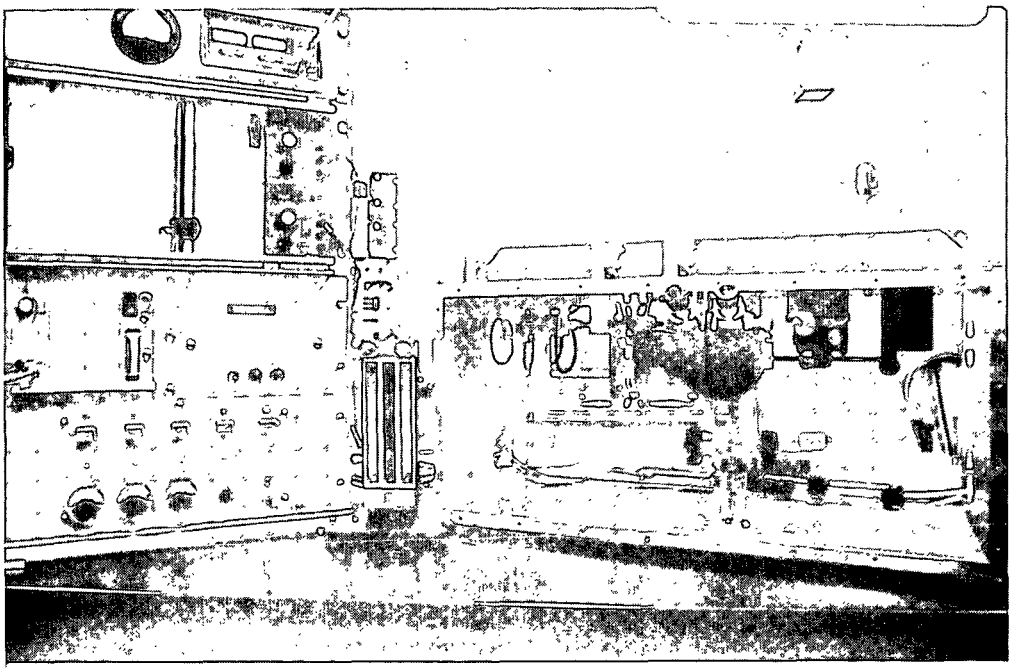


Figure 1. The Fiber Load/Elongation Recorder, Model II.

The core of the instrument is the specimen handling system in the right hand side of the photo. A schematic of this is shown in Fig. 2, where an electronic weighing cell, A, is suspended beneath a mounting plate, B, by means of four flexure springs, C. A dc servo motor, D, turns a differential screw, E, pulling or pushing the weighing cell to apply a tensile or compression load to a specimen mounted between the clamps, F. The right hand clamp may be positioned along the test axis by the compound microscope focusing mechanism, G, and be locked in place by the clamp, H. Specimen extension or compression is measured between this fixed clamp and the opposing, movable clamp. A capacitive displacement transducer, I, supported by the pillar, J, senses the position of the movable clamp.

A stereoscopic microscope is mounted to permit viewing and/or photographing the specimens during mounting and testing. Special jigs and holders are being developed for mounting the specimens in the various configurations desired.

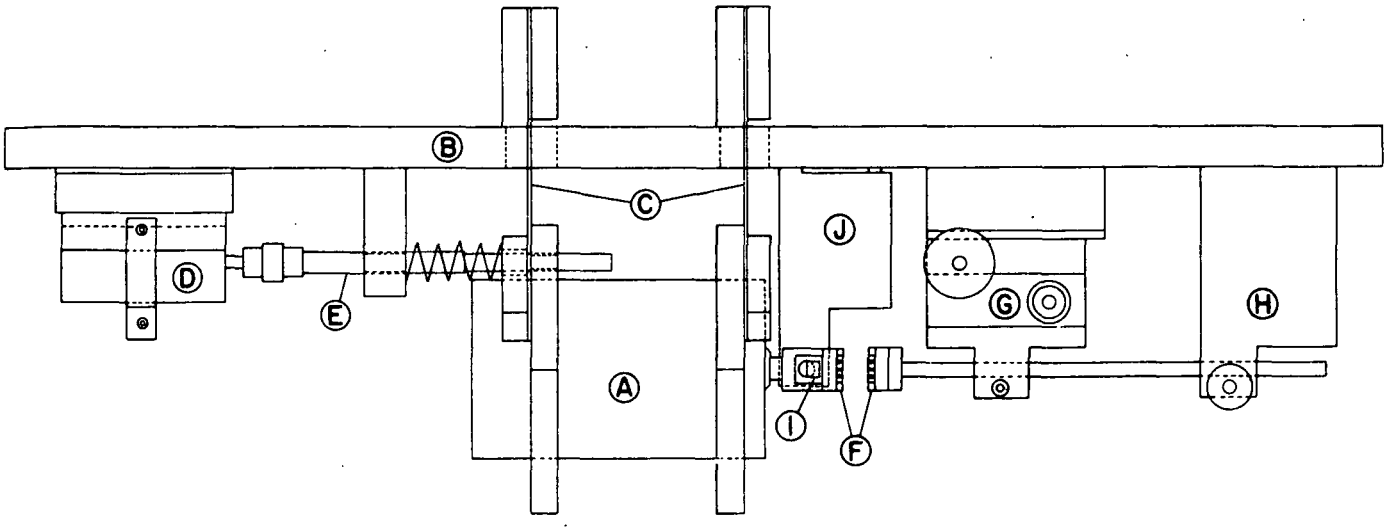


Figure 2. Side view of the Fiber Load/Elongation Recorder, Model II. Scale: 1 in = 5 in. A - electronic weighing cell, B - mounting plate, C - flexure springs, D - dc servo motor, E - differential screw, F - clamps, G - microscope focusing mechanism, H - clamp, I - transducer, and J - pillar.

Dry air and air saturated with moisture are mixed in any desired ratio in the small mixer shown in the center of Fig. 1, then allowed to exit so as to envelope the specimen and set its moisture content. The relative humidity and temperature of the mixed air stream are sensed, then displayed on a readout at the top of the equipment rack shown on the left in Fig. 1.

The signal for driving the dc motor is derived by comparing the signal from the load or elongation sensor with a linear ramp reference voltage. Thus, testing may be done either at constant rate of loading or constant rate of elongation. The ramp generator (at the bottom of the rack in Fig. 1) supplies the ramp and the necessary controls for varying the rate at which the tensile or compression test is performed and setting the load or elongation limits between which the loading and unloading may be cycled.

Calibration of the ramp generator has been completed. As constructed, specimen load and deformation rates are infinitely adjustable between the following limits:

Elongation cell I	(0.05 mm range, 0.05 μm sensitivity)
	0.026 μm/sec to 15 μm/sec
Elongation cell II	(0.25 mm range, 0.25 μm sensitivity)
	0.130 μm/sec to 74 μm/sec
Load cell A	(50 g range, 1 mg sensitivity)
	0.05 g/sec to 30 g/sec
Load cell B	(400 g range, 5 mg sensitivity)
	0.42 g/sec to 242 g/sec

The measured load and elongation signals are applied to an x-y recorder mounted in the rack. They may, of course, also be fed to a digital processor when appropriate.

It has been found that the pitch of the original cut-thread lead screw is somewhat nonuniform. As a result, a small "jerk" is occasionally recorded on the load/elongation curve of even a smoothly deforming specimen, such as a wire spring. A precision-ground lead screw has been ordered to remedy this. Delivery is expected by mid-October.

Current efforts are being directed to the development of fixtures and techniques for measuring fiber-fiber bond strengths according to the configuration shown in Fig. 3.

This procedure will then be used for bond strength measurements at low and high moisture contents needed as part of the internal strength enhancement project (Project 3526).

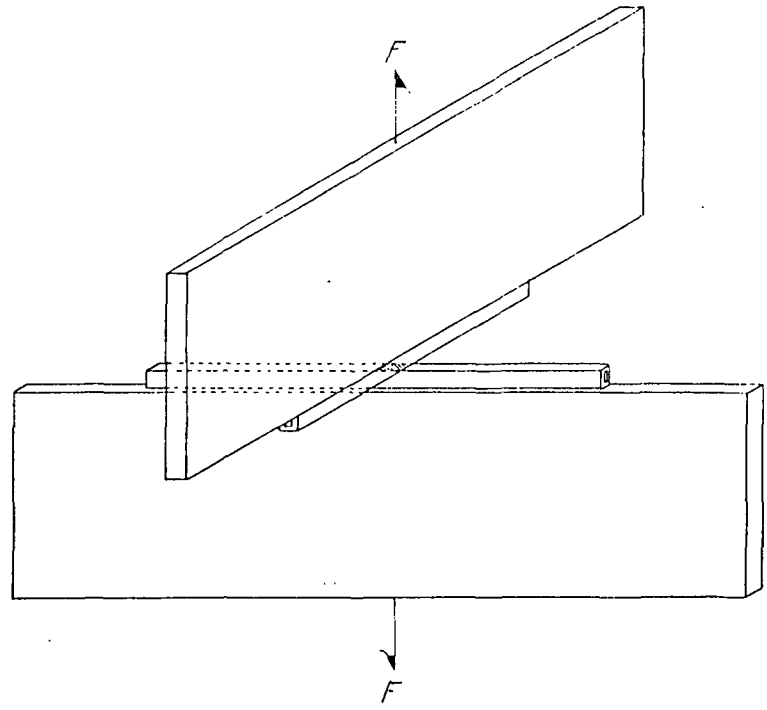


Figure 3. Schematic of wood fibers bonded to glass plates and positioned for fiber-fiber bond strength measurement.

Work will continue with the development of other fixtures needed to measure the additional properties listed on page 107.

K. W. Hardacker
9/13/85

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3526

FUNDAMENTALS OF INTERNAL STRENGTH ENHANCEMENT

October 22, 1985

PROJECT TITLE: Fundamentals of Internal Strength Enhancement

Date: 9/10/85
Budget: $220,000
Period Ends: 6/30/86
Project No.: 3526

PROJECT STAFF: R. A. Stratton, J. J. Becher

PRIMARY AREA OF INDUSTRY NEED: Properties related to end use

PROGRAM AREA: Moisture tolerant, superior strength paper and board

PROGRAM GOAL: Bring new attributes to fiber based products

PROJECT OBJECTIVE:

To improve internal strength and moisture tolerance in paper and paperboard. The short terms goals are to establish those parameters fundamental to inter-fiber and intra-fiber bonding in conventional and ultra high yield pulps and to control these parameters, if possible, by chemical or mechanical treatments.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

(1) Work with the duo-polymer systems described in Progress Report One was extended to higher yield pulps which differed in pulping procedures and wood source. Both additive combinations [carboxymethyl cellulose-polyamide polyamine epichlorohydrin (CMC/PAE)] and polyacrylic acid/PAE (PAA/PAE) were found to improve the strength properties of a 57% yield classified softwood unbleached kraft to levels which were greater than those of the 48% yield kraft controls. Extending this study to an 88-90% yield softwood TMP revealed that CMC/PAE was effective in this pulp.

(2) Pectins from several sources were examined for sorptive properties in an average yield softwood unbleached kraft. While several of these products were adsorbed to some extent, evidence available at this time indicates that they are ineffective as fiber bonding agents; however, this work is incomplete.

(3) The effects of treated and untreated fines on the strength properties of the TMP are under study.

(4) Chemical analysis of polymer-fiber bonding mechanisms is continuing.

(5) Techniques for forming bonded fiber pairs were improved. The use of the vertical polarized light technique to measure bond area was further developed.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

(1) Polymer combinations including polystyrene sulfonic acid (PSFA)/polyamide polyamine epichlorohydrin (PAE) and alginate/PAE provided significant

improvements in strength properties over the controls in a 57% yield classified softwood unbleached kraft pulp but these combinations were generally less effective than the previously tested carboxymethyl cellulose (CMC)/PAE and polyacrylic acid (PAA)/PAE combinations.

(2) The effectiveness of pectins in an average-yield classified softwood unbleached kraft pulp was greatly enhanced by the addition of PAE to the extent that the resulting strength properties approached, equalled, or exceeded those of CMC/PAE or PAA/PAE depending upon the polymer ratio and addition level. However, cost would eliminate pectins from further consideration at this time.

(3) A study of fines and polymer combinations in a softwood TMP indicated that the readdition of untreated fines to the classified pulp produced tensile strength levels which approached but did not match those of the original whole pulp except in wet tensile and dry Et. The addition of polymer bonding agents to the classified (long) fiber fraction was generally more effective than addition to the fines fraction. Combining CMC/PAE-treated classified fibers and fines to form a whole treated pulp was, in most cases, more effective than adding the same amount of polymer to the original untreated whole pulp. In general, CMC/PAE was more effective than PAA/PAE in this 88% yield pulp.

(4) Diffuse reflectance FTIR analysis of handsheets treated with PAE and polymer combinations containing PAE indicates that ester formation and hence, covalent bonding occurred with several pulps varying in yield and wood source.

(5) Repulpability studies using handsheets from a 49% yield whole unbleached softwood kraft showed that the Thwing formation values of papers treated with CMC/PAE of PAA/PAE were equivalent to the blank controls and those treated with PAE alone after 5 or 7 minutes of intensive mechanical and chemical treatment.

(6) Initial attempts to use the new fiber load-elongation instrument (FLER II) to measure the strength of single fiber-fiber bonds were unsuccessful. New techniques are being developed.

(7) Techniques were further developed to measure the bending modulus of paper and board samples as a function of relative humidity using the vibrating reed method. A humidity control system was built which will allow measurements to be made in the range 0-95% RH at room temperature. Studies on the effect of air damping and strain amplitude showed that only minor corrections to the modulus were required.

PROJECT TITLE: Fundamentals of Internal Strength Enhancement

PROJECT STAFF: R. A. Stratton/J. J. Becher

PRIMARY AREA OF INDUSTRY NEED: Properties related to end use

PROGRAM AREA: Moisture tolerant, superior strength paper and board

Date: 6/1/84
Budget: $220,000
Period Ends: 6/30/86
Project No.: 3526
Approved by VP-R:

PROGRAM GOAL: Bring new attributes to fiber based products

PROJECT OBJECTIVE:

To improve internal strength and moisture tolerance in paper and paperboard. The short term goals are to establish those parameters fundamental to inter-fiber and intra-fiber bonding in conventional and ultra high yield pulps and to control these parameters, if possible, by chemical or mechanical treatments.

PROJECT RATIONALE:

Major limitations of paper and board for many uses are low internal bond strength and poor moisture tolerance. Improved internal strength and enhanced moisture resistance would allow a number of present grades to be produced using less fiber and would also allow new end uses to be developed.

Size pressing is one way currently used to enhance internal strength. If this operation could be eliminated, or substantially changed to improve paper machine runnability, paper machine productivity could be also significantly improved.

RESULTS TO DATE:

PART ONE: Improved bonding via chemical additives.

Results through June, 1984 were presented in Progress Report One. In brief review, two duopolymer combinations, i.e., CMC/PAE and PAA/PAE were found to be very effective in improving the dry, moist, and wet tensile properties of several classified southern pine unbleached kraft pulps prepared at the Institute. The results suggested that synergistic effects with respect to polymer effectiveness had occurred. Chemical analysis indicated that covalent bonds were formed in the presence of the polymer combinations.

The study of polymer combinations incorporating PAE as the cationic component was extended to include other anionic materials such as sodium polystyrene sulfonate (PSFA), sodium alginate and pectins. While PSFA and sodium alginate produced substantial improvements over the blank controls, they did not match the overall performance of CMC/PAE and PAA/PAE. On the other hand, fruit pectin/PAE blends equalled or exceeded CMC/PAE in some cases. However, the cost of pectins was considered prohibitive, thus, further work with these materials has been terminated for the present.

The effect of bonding agents and fines content has been examined in a softwood TMP of 88-90% yield. The results show that the bonding agents, particularly CMC/PAE, are generally more effective when added to the classified (long-fiber) fraction than addition to the fines fraction. This tendency for the bonding agents to be more effective in classified pulps has been noted previously. With a few exceptions, combining CMC/PAE - treated classified fibers and fines to form a whole pulp produced higher dry, moist, and wet strength than adding the same amount of bonding agent to the whole pulp. Moist strength properties are being remeasured in light of recent indications that sheet moisture content at high humidity varies with the type and amount of polymeric bonding agent used in the presence of fines. The repulpability of unbleached kraft handsheets containing CMC/PAE and PAA/PAE was found to be comparable to those containing PAE alone.

Diffuse reflectance FTIR analysis of polymer treated handsheets from several pulps indicates that covalent bonding occurs in these systems.

PART TWO: Fundamentals of bonding.

Techniques were developed to study the details of the fracture of the bond between two single fibers. They consisted of:

a) forming the fiber/fiber bond.
b) measuring the bond area using vertical polarized illumination.
c) determining the bond strength, and
d) determining the locus of failure of the bond using the scanning electron microscope.

Results showed a bimodal distribution of bond strengths. In separate experiments bonds were found to fail either between the two fibers with no surface damage or within the wall of one or both of the fibers.

A vibrating reed instrument has been developed to measure the bending modulus of paper and board samples. A range of temperatures from ambient to 200°C and a range of relative humidities from 0 to 95% at room temperature can be covered.

PLANNED ACTIVITY FOR THE PERIOD:

This project is complementary to two expansion projects proposed in 1982: One concerned with moisture tolerant products and the other high yield pulps. In addition, another current project (3527) is concerned with the development of instrumentation which will eventually be used in this project.

The following activities are planned for this fiscal year.

Part One:

(1) The study of polymeric bonding agents will be continued. While several anionic/cationic polymer combinations have been found to be quite effective, other materials of this nature will be given consideration based on chemical structure and known properties.

(2) Bonding agents producing positive results thus far will be tested further in average- and high-yield pulps including a softwood chemimechanical in addition to the TMP.

(3) The role of fines in the use of chemical additives will be examined further. The effect of polymer addition on fines retention and sheet moisture content will be important aspects of this study.

(4) The study of bonding mechanisms will be pursued based primarily on diffuse reflectance FTIR analysis. This applies in particular to the duopolymer additives but is not necessarily limited to these materials.

Part Two:

(1) Failure of single fiber/fiber bonds will be examined in detail, with correlations expected among bonded area, bond strength, and locus of failure.

(2) Effective chemical additives identified in Part One will be used in forming single fiber/fiber bonds, whose failure will then be examined as above.

(3) Studies on the effects of pulp yield and refining on mode of bond failure will begin.

STATUS REPORT

FUNDAMENTALS OF INTERNAL STRENGTH ENHANCEMENT

Project 3526

PART ONE: Improved Bonding via Chemical Additives.

INTRODUCTION

Results through June, 1984 were presented in Progress Report One. In brief review, two duopolymer combinations i.e., CMC/PAE and PAA/PAE were found to be very effective in improving the dry, moist, and wet tensile properties of average yield classified southern pine unbleached kraft pulps prepared at the Institute. The results suggested that synergestic effects with respect to additive effectiveness had occurred. Chemical analysis indicated that covalent bonds were formed in the presence of the polymeric additives.

In pursuing work with the polymer combinations, CMC/PAE and PAA/PAE were evaluated in higher yield pulps which differed in pulping process and wood source. The pulps included a 57% yield classified softwood unbleached kraft and an 88% yield classified softwood TMP. Increasing the yield of the unbleached kraft pulp from 48 to 57% resulted in a substantial reduction in tensile properties. However, addition of either CMC/PAE or PAA/PAE increased dry and moist breaking length to levels which were equivalent to or greater than those of the 48% yield controls. The CMC/PAE combination was also found to be quite effective in the 88% yield TMP whereas PAA/PAE failed to provide a consistent advantage over PAE alone. The potential of pectins as bonding agents for an average yield softwood unbleached kraft was examined in a series of preliminary screening tests. The results indicated that moderate retentions for some fruit pectins were attained at an addition level of 2% but they proved to be of little value as bonding agents by themselves. Further evaluation of pectins and other anionic polymers is included in this report.

RESEARCH RESULTS

In the descriptions that follow, it should be noted that 2.5-gram Noble & Wood handsheets were formed in tap water in all cases. Unless stated otherwise, the handsheets were pressed 5 minutes at 50 psig and drum dried for seven minutes at 225°F. The handsheets were tested for dry, moist (about 91-93% RH), and wet tensile properties as in previous studies.

Work with duopolymer systems was extended to include several anionic carboxyl-bearing polymers in combination with PAE. Most of this work was carried out with the classified 57% yield southern pine unbleached kraft pulp. In addition to the reference PAE and the CMC/PAE and PAA/PAE standards, combinations of sodium polystyrene sulfonate/PAE and sodium alginate/PAE were evaluated over a range in additive ratio with a maximum addition level of 1.6% based on fiber. Results for this series are presented in Table 1 and Figs. 1-6. Note that Table 1 also includes previously described results pertaining to the effects of sheet density and the presence of sizing agents on sheet properties. It becomes evident in examining these data that the optimum anionic polymer/PAE ratio is 0.1 to 0.2. Since the addition level was increased with polymer ratio (PAE dosage constant), the maxima achieved at lower ratios translates to economic advantages. It is evident that combining PAE with the anionic polymers increases strength to the point where the resulting strength equals or exceeds that of 1.5% PAE in dry and wet tensile properties. However, in general, the strength afforded by these anionic/cationic polymer combinations did not match that of CMC/PAE or PAA/PAE. This would apply in particular to set no. 6 which utilizes pearl cornstarch in combination with reduced levels of PAE and PAA and thereby provides a cost advantage.

Table 1. The effectiveness of additives in a 57% yield classfied unbleached softwood kraft pulp, kappa no. 102.3.

Set No.	Additives, % Based on Fiber	Wet Pressing Conditions	Basis Weight, g/m²	Thick-ness, µm	Apparent Density g/cc	Dry Strength Properties: Breaking Length Km	SD	TEA Kgm/m²	SD	Et Kg/cm	SD	Stretch %	SD
1	Blank controls-1	Normal[a]	62.4	208	0.3	1.54	0.144	0.64	0.143	172	14.9	1.0	0.116
2	Blank controls-2	Flat pressed 15 min at 100 psig	62.7	182	0.345	1.66	0.134	0.805	0.18	179	15.4	1.2	0.149
3	PAE,1.0	Normal	62.1	194	0.32	2.8	0.192	2.3	0.339	195	16.1	1.94	0.161
4	PAE,1.5	Normal	62.3	196	0.318	2.85	0.076	2.03	0.244	234	13.4	1.71	0.188
5	PAE 0.5;PAA,0.1	Normal	62.6	188	0.332	2.88	0.153	2.26	0.366	219	14.3	1.84	0.236
6	1:1 starch:PAE,1.0;PAA,0.1	Normal	63.1	175	0.361	4.15	0.294	4.48	0.584	268	21.7	2.52	0.239
7	PAE,1.0;CMC,0.4	Normal	62.0	182	0.341	3.23	0.239	2.97	0.68	228	9.3	2.2	0.355
8	PAE,1.0;PAA,0.2[b]	Normal	64.2	178	0.36	4.03	0.323	3.85	1.055	304	25.3	2.23	0.45
9	PAE,1.0;PAA,0.2[c]	Normal	63.2	187	0.337	3.39	0.302	3.03	0.609	263	17.6	2.12	0.279
10	PAE,1.0:PAA,0.2[d]	Normal	63.4	199	0.318	2.54	0.175	1.75	0.202	218	12.3	1.66	0.102
11	PAE,1.0;PAA,0.2;alum,0.5; dispersed size,0.25d	Normal	62.7	200	0.314	2.35	0.191	1.65	0.269	204	16.2	1.68	0.122
12	PAE,1.0;PAA,0.2;alkenyl succinic anhydride,0.25b	Normal	61.9	165	0.375	4.47	0.202	4.8	0.538	310	8.2	2.61	0.193
13	PSFA[e] 0.6	Normal	64.9	210	0.309	1.42	0.088	0.592	0.037	176	23.0	0.989	0.069
14	Alginate[f],0.6	Normal	62.9	211	0.298	1.27	0.07	0.485	0.082	152	2.1	0.946	0.092
15	PAE,1.0;PSFA,0.1	Normal	61.5	188	0.326	3.13	0.218	2.47	0.452	255	14.6	1.9	0.203
16	PAE,1.0;PSFA,0.2	Normal	61.4	189	0.324	3.14	0.163	2.57	0.558	242	20.2	1.96	0.315
17	PAE,1.0;PSFA,0.4	Normal	62.4	200	0.313	2.68	0.154	1.81	0.285	235	15.9	1.62	0.135
18	PAE,1.0;PSFA,0.6	Normal	61.3	198	0.309	2.56	0.102	1.79	0.291	225	15.5	1.69	0.223
19	PAE,1.0;alginate,0.05	Normal	67.6	210	0.322	2.34	0.257	1.47	0.428	234	8.9	1.4	0.238
20	PAE,1.0;alginate,0.10	Normal	62.8	184	0.341	3.16	0.173	2.58	0.538	262	8.4	1.94	0.266
21	PAE,1.0;alginate,0.20	Normal	64.8	198	0.328	3.11	0.157	2.53	0.321	258	14.3	1.86	0.14
22	PAE,1.0;alginate,0.40	Normal	62.6	193	0.324	2.79	0.245	2.01	0.45	237	5.0	1.71	0.229
23	PAE,1.0;alginate,0.60	Normal	64.7	201	0.322	3.03	0.094	2.48	0.299	255	20.4	1.88	0.173

[a]Flat pressed 5 min at 50 psig.
[b]pH not controlled; final pH 8-9.
[c]pH adjusted to 5 with sulfuric acid.
[d]pH adjusted to 5 with alum.
[e]PSFA = polystyrene sulfonic acid.
[f]Sodium alginate, medium viscosity.

Table 1. Continued...

Set No.	Additives, % Based on Fiber	Moist Strength Properties: Breaking Length Km	SD	TEA Kgm/m²	SD	Et Kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length Km	SD	Wet Tensile Factor	Sizing Water Drop Sec.
1	Blank controls-1	0.657	0.031	0.412	0.041	71.5	11.7	1.44	0.193	1.0	0.018	0.004	1.0	Instantaneous
2	Blank controls-2	0.682	0.036	0.499	0.057	65.8	17.1	1.6	0.12	1.04	0.069	0.008	3.83	Instantaneous
3	PAE,1.0	1.59	0.11	1.93	0.142	85.3	15.7	2.98	0.27	2.42	0.721	0.043	40.1	Instantaneous
4	PAE,1.5	1.57	0.107	2.02	0.226	76.0	6.6	3.42	0.084	2.39	0.739	0.029	41.0	Instantaneous
5	PAE 0.5;PAA,0.1	1.85	0.137	3.13	0.505	97.3	16.6	3.24	0.306	2.82	0.762	0.047	42.3	Instantaneous
6	1:1 starch:PAE,1.0;PAA,0.1	2.24	0.173	4.23	0.812	109.0	7.97	3.79	0.308	3.41	1.26	0.105	70.0	Instantaneous
7	PAE,1.0;CMC,0.4	1.87	0.261	2.47	0.674	95.8	5.7	3.42	0.541	2.85	0.994	0.041	55.2	Instantaneous
8	PAE,1.0;PAA,0.2[b]	2.26	0.112	3.26	0.179	108.0	18.9	3.65	0.34	3.44	1.13	0.058	62.5	Instantaneous
9	PAE,1.0;PAA,0.2[c]	1.97	0.174	2.98	0.36	95.5	15.0	3.6	0.08	3.0	0.913	0.09	50.7	Instantaneous
10	PAE,1.0:PAA,0.2[d]	1.38	0.082	1.79	0.177	85.3	13.3	2.92	0.164	2.1	0.721	0.046	40.1	Instantaneous
11	PAE,1.0;PAA,0.2;alum,0.5; dispersed size,0.25d	1.32	0.085	1.52	0.114	85.0	22.9	2.76	0.12	2.01	0.66	0.06	36.7	1800+
12	PAE,1.0;PAA,0.2;alkenyl succinic anhydride,0.25b	2.61	0.19	4.01	0.534	98.8	6.15	4.0	0.26	3.97	1.08	0.086	60.0	1800+
13	PSFA[e] 0.6	0.379	0.028	0.342	0.022	40.6	3.61	1.72	0.061	0.577	0.046	0.009	2.55	
14	Alginate[f],0.6	0.378	0.043	0.336	0.059	39.8	2.61	1.67	0.194	0.575	0.0434	0.003	2.41	
15	PAE,1.0;PSFA,0.1	1.44	0.079	2.22	0.272	53.3	4.16	3.8	0.237	2.19	0.836	0.05	46.4	
16	PAE,1.0;PSFA,0.2	1.53	0.076	2.28	0.16	60.2	3.19	3.8	0.135	2.33	0.826	0.061	45.9	Instantaneous
17	PAE,1.0;PSFA,0.4	1.12	0.078	1.8	0.295	45.1	3.44	3.78	0.19	1.7	0.7	0.023	38.9	Instantaneous
18	PAE,1.0;PSFA,0.6	1.09	0.081	1.67	0.3	44.0	3.69	3.54	0.406	1.66	0.612	0.043	34.0	Instantaneous
19	PAE,1.0;alginate,0.05	1.01	0.027	1.42	0.105	47.8	1.22	3.14	0.109	1.54	0.639	0.05	35.5	
20	PAE,1.0;alginate,0.10	1.37	0.139	1.94	0.328	59.5	3.22	3.51	0.374	2.08	0.902	0.049	50.1	
21	PAE,1.0;alginate,0.20	1.44	0.115	2.05	0.203	62.6	7.22	3.52	0.112	2.19	0.798	0.032	44.3	
22	PAE,1.0;alginate,0.40	1.14	0.037	1.57	0.084	40.3	3.8	3.64	0.252	1.74	0.801	0.085	44.5	
23	PAE,1.0;alginate,0.60	1.19	0.073	1.72	0.249	50.4	1.85	3.49	0.277	1.81	0.8	0.018	44.4	

[a]Flat pressed 5 min. at 50 psig.
[b]pH not controlled; final pH 8-9.
[c]pH adjusted to 5 with sulfuric acid.
[d]pH adjusted to 5 with alum.
[e]PSFA = polystyrene sulfonic acid.
[f]Sodium alginate, medium viscosity.

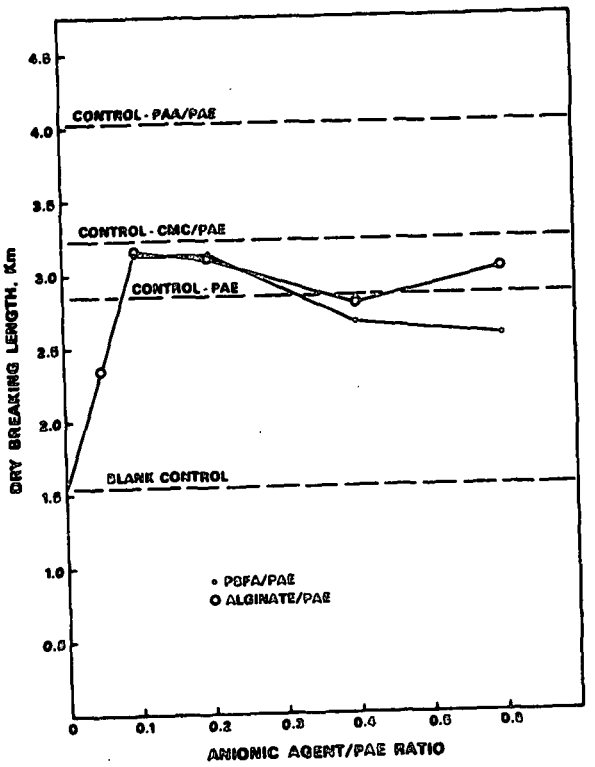


Figure 1. The effect of additive ratio on dry breaking length (57% yield softwood unbleached kraft - classified).

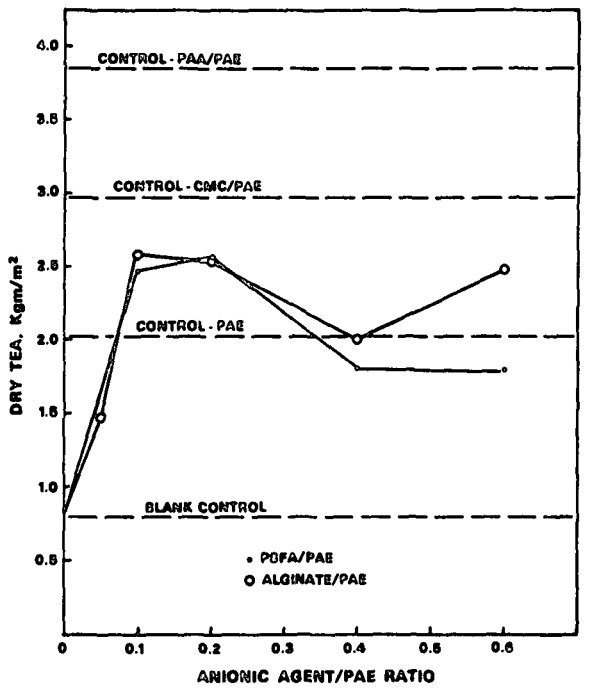


Figure 2. The effect of additive ratio on dry TEA (57% yield softwood unbleached kraft - classified).

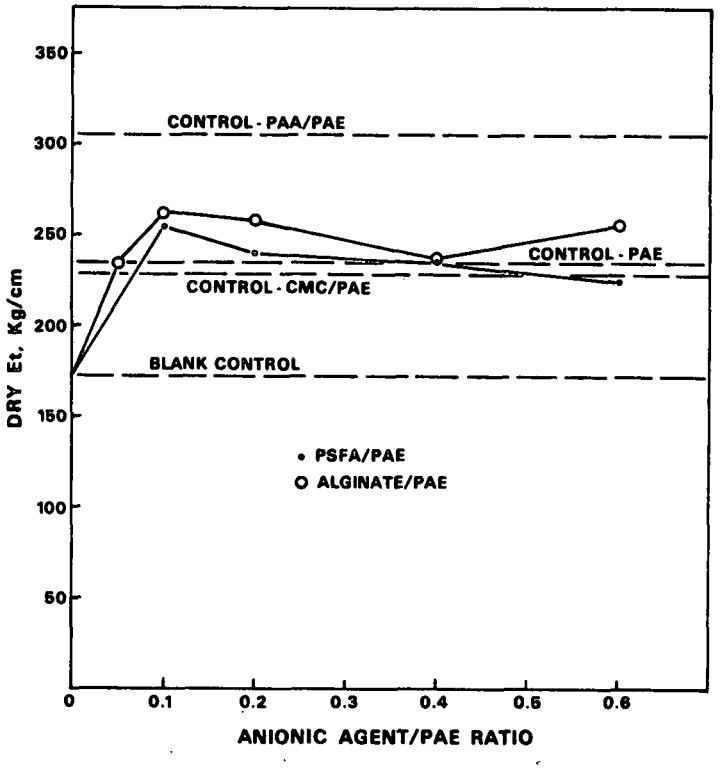


Figure 3. The effect of additive ratio on dry Et (57% yield softwood unbleached kraft - classified).

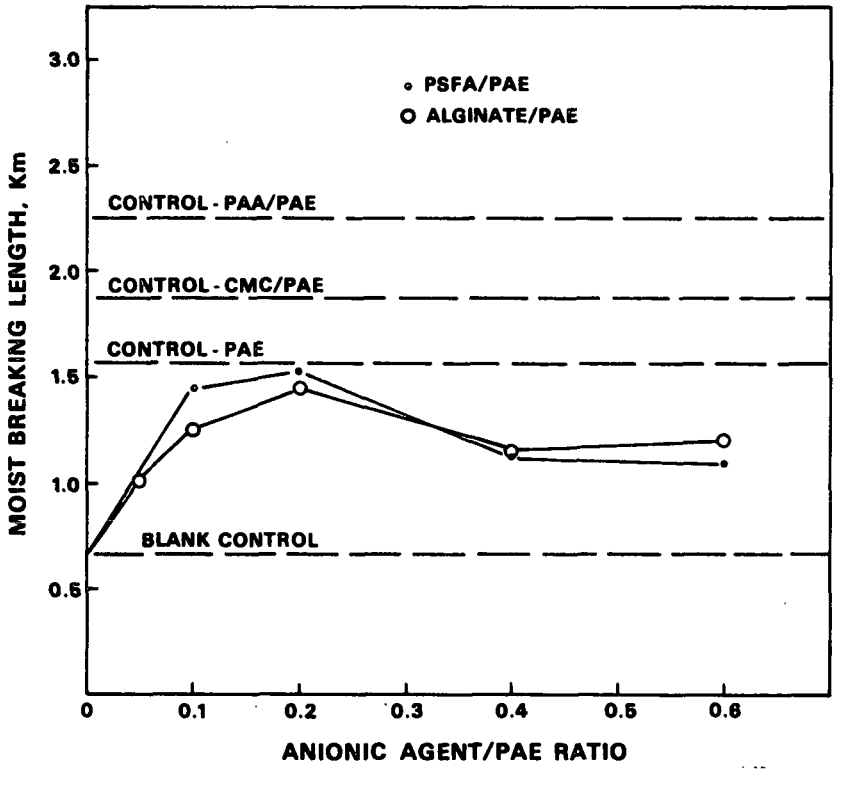


Figure 4. The effect of additive ratio on moist breaking length (57% yield softwood unbleached kraft - classified).

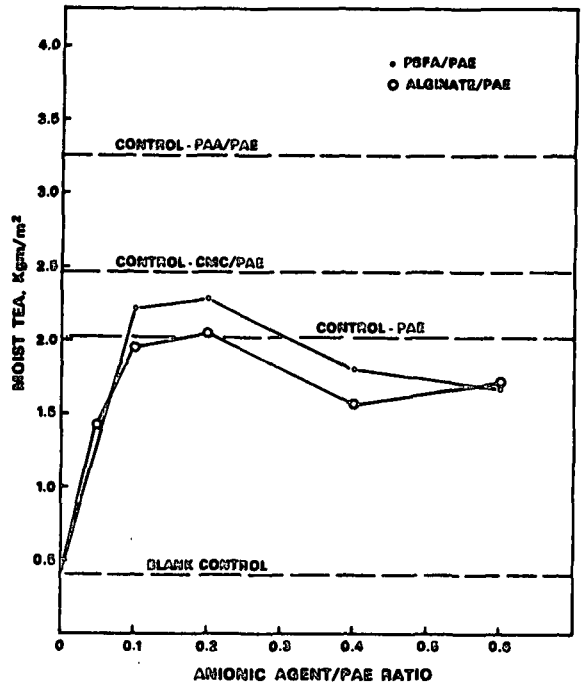


Figure 5. The effect of additive ratio on moist TEA (57% yield softwood unbleached kraft - classified).

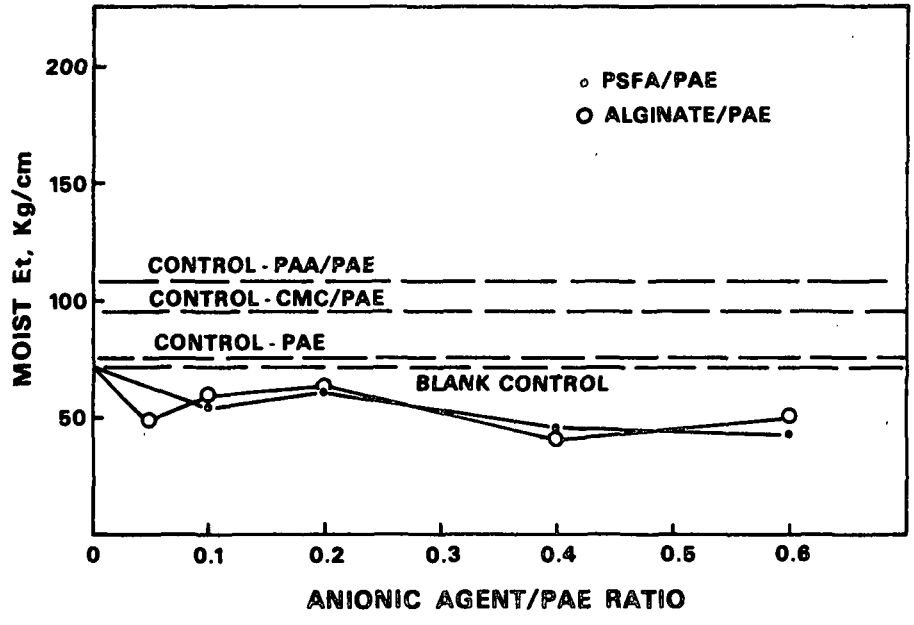


Figure 6. The effect of additive ratio on moist Et (57% yield softwood unbleached kraft - classified).

Other results of interest in Table 1 (sets 11 & 12) indicate that either dispersed rosin size or synthetic size can be used to produce water resistance in handsheets containing PAA/PAE. However, the dispersed rosin size reduced strength properties whereas the synthetic size tended to enhance strength in most cases. This may be due, in part, to the presence of starch in the synthetic size. Alum greatly reduces the effectiveness of the PAA/PAE system due possibly to an excess of cationic change and/or destabilization of the polyacrylic acid.

The properties and relative effectiveness of pectins are presented in Tables 2-4 and Figs. 7-12. In this case a beaten and classified unbleached kraft pulp of 49% yield was utilized in adsorption and handsheet tests. Total carbon (TC) content was used as the basis for determining adsorbed pectin.

Table 2. The sorptive properties of pectins and related materials on southern pine unbleached kraft[a].

Product No.	Identification	Solids Content, %	Concentration of Filtrate From Pulp + Pectin, T.C., PPM			TC of Pectin, ppm	Adsorbed Pectin, T.C.	Pectin Adsorbed, % Based on Pectin in Solution
			Test 1	Test 2	Av.			
1	Grapefruit pectin, 2nd batch	87.67	99.9	9.3	99.6	75.3	0.3	0.398
2	Pectin from citrus fruits;No. P-9135	90.46	97.5	99.3	98.4	77.5	3.7	4.77
3	Sunkist polygalacturonic acid,No. 3491	88.26	34.5	33.8	34.15	14.6	5.25	34.5
4	Polygalacturonic acid from orange,P 3889	91.46	30.8	30.3	30.6	8.2	2.2	26.8
5	Apple pectin	91.2	101.0	101.0	101.0	77.3	0.9	1.2
6	Sugar beet pectin	90.72	95.6	97.4	96.5	75.4	3.5	4.64
7	Sapote 58	91.08	111.0	112.0	111.5	83.7	-3.2	-------
8	Gum Tragacanth;No. G-1128,Grade III	89.62	81.5	81.5	81.5	51.1	-5.8	-------
9	Gum Ghatti,No. G-03878;Lot 87C-0084	88.74	89.3	89.9	89.6	61.6	-3.4	-------
10	Gum Arabic;No. G-9752	87.94	109.0	110.0	109.5	80.9	-4.0	-------
11	Guar gum;No. G-4129;Lot 21F-0521	89.32	69.6	71.3	70.45	56.6	10.75	19.0
12	Karaya gum	82.59	90.7	93.4	92.1	64.6	-2.9	-------

[a]49% yield, beaten to 370 CSF then classified.

Notes: The pH in this retention study was 4.0-4.5.
T.C. = total carbon.
T.C. of pulp filtrate was 24.6 ppm.

Table 3. A comparison of pectins as bonding agents for southern pine unbleached kraft, (49% yield-classified).

Set No.	Additives, % Based on Fiber	Basis Weight g/m2	Thick-ness, µm	Apparent Density g/cc	Dry Strength Properties: Breaking Length Km	SD	TEA Kgm/m	SD	Et Kg/cm	SD	Stretch %	SD
24	Blank controls	63.1	158	0.399	3.93	0.212	4.37	0.282	279	14.7	2.58	0.052
25	PAE,1.0	67.3	174	0.387	5.73	0.279	6.92	0.847	450	16.9	2.76	0.241
26	PAE,1.5	71.7	166	0.433	6.12	0.794	8.99	1.166	412	58.4	3.13	0.216
27	PAE,1.0;CMC,0.4	63.9	152	0.419	7.79	0.372	11.2	1.19	355	16.0	3.58	0.232
28	PAE,1.0;PAA,0.2	71.9	167	0.43	6.48	0.109	9.05	0.851	379	50.5	3.0	0.249
29	1:1 starch:PAE,1.0;PAA,0.1	70.5	164	0.428	6.13	0.549	9.16	1.29	375	48.6	3.27	0.166
30	Grape fruit pectin, 2.0	68.8	167	0.411	3.61	0.343	3.59	0.648	307	22.6	2.12	0.195
31	Pectin from citrus fruits;No. P-9135,2.0	69.0	167	0.413	3.99	0.285	4.43	0.634	312	16.8	2.37	0.166
32	Sunkist polygalacturonic acid,No. 3491,2.0	72.8	176	0.413	3.95	0.351	4.84	0.689	337	33.8	2.46	0.149
33	Polygalacturonic acid from orange;No. 3889,2.0	62.3	158	0.345	3.87	0.269	3.74	0.559	270	56.7	2.28	0.206
34	Sugar beet pectin,2.0	67.9	167	0.406	3.47	0.379	3.28	0.594	334	38.7	2.0	0.163
35	Guar gum No. 4129;Lot 21-F-0521,2.C	64.5	153	0.42	4.48	0.194	5.54	0.53	326	19.1	2.82	0.189

Set No.	Additives, % Based on Fiber	Moist Strength Properties: Breaking Length Km	SD	TEA Kgm/m2	SD	Et Kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length Km	SD	Wet Tensile Factor
24	Blank controls	1.98	0.114	2.68	0.186	109	6.9	3.39	0.073	1.0	0.158	0.012	1.0
25	PAE,1.0	3.37	0.359	5.99	0.627	148	11.6	4.32	0.277	1.7	1.69	0.044	10.69
26	PAE,1.5	3.79	0.327	6.65	0.492	131	11.2	4.59	0.121	2.0	1.92	0.119	12.15
27	PAE,1.0;CMC,0.4	4.86	0.311	9.05	1.076	150	23.4	5.16	0.253	2.45	2.27	0.2	14.37
28	PAE,1.0;PAA,0.2	4.05	0.331	7.51	0.96	172	21.4	4.41	0.206	2.05	1.81	0.062	11.45
29	1:1 starch:PAE,1.0;PAA,0.1	3.9	0.268	6.96	0.797	190	23.7	4.29	0.262	1.97	1.35	-----	8.54
30	Grape fruit pectin,2.0	2.1	0.236	3.17	0.54	163	13.3	3.3	0.193	1.06	0.13	0.022	0.82
31	Pectin from citrus fruits;No. P-9135,2.0	2.08	0.05	2.84	0.198	159	8.3	3.05	0.165	1.05	0.115	0.0126	0.73
32	Sunkist polygalacturonic acid,No. 3491,2.0	2.25	0.294	3.45	0.744	179	22.0	3.18	0.277	1.14	0.14	0.027	0.89
33	Polygalacturonic acid from orange;No. 3889,2.0	2.13	0.124	2.94	0.186	139	17.0	3.37	0.073	1.08	0.148	0.0081	0.94
34	Sugar beet pectin, 2.0	1.95	0.128	2.63	0.192	162	11.1	2.94	0.059	0.98	0.132	0.015	0.84
35	Guar gum No. 4129;Lot 21-F-0521,2.0	2.39	0.077	3.36	0.062	174	12.5	3.36	0.084	1.2	0.166	0.0076	1.05

Table 4. The effect of selected pectins on strength properties of unbleached southern pine kraft; yield 49.2%; beaten and classified.

Set No.	Additives, % Based on Fiber	Basis Weight g/m²	Thick-ness µm	Apparent Density g/cc	Dry Strength Properties: Breaking Length Km	SD	TEA Kgm/m2	SD	Et Kg/cm	SD	Stretch %	SD
24	Blank controls	63.1	158	0.399	3.93	0.212	4.37	0.282	279	14.7	2.58	0.052
25	PAE,1.0	67.3	174	0.387	5.73	0.279	6.92	8.47	350	16.9	2.76	0.244
26	PAE,1.5	71.7	166	0.433	6.12	0.794	8.99	1.166	412	58.4	3.13	0.266
27	PAE,1.0;CMC,0.4	63.9	152	0.419	7.79	0.372	11.2	1.19	355	16.0	3.58	0.232
28	PAE,1.0;PAA,0.2	71.9	167	0.43	6.48	0.109	9.05	0 .851	379	50.5	3.0	0.249
29	1:1 starch;PAE,1.0;PAA, 0.1	70.5	164	0.428	6.13	0.549	9.16	1.29	375	48.6	3.26	0.166
36	Pectin P-9135a,2.0;alum to pH 4.0	72.9	172	0.423	3.8	0.11	4.36	0.385	305	62.2	2.36	0.157
37	Pectin P-9135a,2.0;alum to pH 5.5	71.0	170	0.419	3.92	0.364	4.35	0.892	358	24.1	2.24	0.263
38	Pectin P-9135a,2.0;alum to pH 7.0	66.5	162	0.412	3.84	0.29	3.84	0.852	315	20.0	2.19	0.232
39	PAE,1.0;pectin P-9135,0.1	67.6	162	0.417	6.31	0.317	8.27	0.411	382	20.8	3.02	0.038
40	PAE,1.0;pectin P-9135,0.2	74.7	172	0.434	6.69	0.495	10.5	1.24	436	28.5	3.27	0.189
41	PAE,1.0;pectin P-9135,0.4	62.8	145	0.434	7.48	0.63	10.8	1.4	375	30.0	3.59	0.165
42	PAE,1.0;pectin P-9135,0.6	67.8	152	0.447	7.58	0.453	12.1	0.99	415	33.1	3.72	0.167
43	PAE,1.0;pectin P-9135,1.0	71.0	156	0.454	7.35	0.372	10.8	1.34	455	11.4	3.26	0.245
44	PAE,1.0;sugar beet pectin,0.1	71.5	169	0.424	5.47	0.694	6.92	1.85	375	21.4	2.73	0.415
45	PAE,1.0;sugar beet pectin,0.4	73.5	172	0.428	6.27	0.226	9.48	0.759	410	10.2	3.23	0.165
46	PAE,1.0;sugar beet pectin,1.0	68.4	160	0.425	6.64	0.538	9.50	1.203	394	24.8	3.28	0.165

Set No.	Additives, % Based on Fiber	Moist Strength Properties: Breaking Length Km	SD	TEA Kgm/m²	SD	Et Kg/cm	SD	Stretch %	SD	Moist Tensile Factor	Wet Breaking Length Km	SD	Wet Tensile Factor
24	Blank controls	1.98	0.114	2.68	0.186	109	6.9	3.39	0.073	1.0	0.158	0.012	1.0
25	PAE,1.0	3.37	0.359	5.99	0.627	148	11.6	4.32	0.277	1.7	1.69	0.044	10.69
26	PAE,1.5	3.79	0.437	6.65	0.492	131	11.2	3.59	0.121	1.0	1.92	0.119	12.15
27	PAE,1.0;CMC, 0.4	4.86	0.311	9.05	1.076	150	23.4	5.1	0.253	2.45	2.27	0.2	14.37
28	PAE,1.0;PAA, 0.2	4.05	0.331	7.51	0.96	172	21.4	4.41	0.206	2.05	1.81	0.062	11.45
29	1:1 starch;PAE,1.0;PAA, 0.1	3.9	0.268	6.96	0.797	190	23.7	4.29	0.262	1.97	1.35		8.54
36	Pectin P-9135a,2.0;alum to pH 4.0	2.18	0.065	3.75	0.132	160	8.7	3.52	0.181	1.1	0.143	0.0028	0.91
37	Pectin P-9135a,2.0;alum to pH 5.5	2.05	0.129	3.25	0.133	138	12.0	3.51	0.088	1.01	0.149	0.021	0.94
38	Pectin P-9135a,2.0;alum to pH 7.0	1.99	0.141	3.01	0.298	123	7.1	3.6	0.149	1.0	0.138	0.011	0.87
39	PAE,1.0;pectin P-9135,0.1	3.78	0.169	7.61	0.668	135	12.2	4.59	0.228	1.91	1.91	0.126	12.09
40	PAE,1.0;pectin P-9135,0.2	4.04	0.318	7.69	1.059	131	10.4	5.03	0.314	2.04	1.95	0.101	12.34
41	PAE,1.0;pectin P-9135,0.4	4.78	0.392	8.02	0.808	140	14.0	4.93	0.169	2.4	2.27	0.186	14.37
42	PAE,1.0;pectin P-9135,0.6	4.79	0.339	8.24	1.103	153	9.5	4.88	0.269	2.42	2.32	0.225	14.68
43	PAE,1.0;pectin P-9135,1.0	4.73	0.287	8.76	1.279	138	9.4	5.08	0.361	2.39	2.32	0.097	14.68
44	PAE,1.0;sugar beet pectin,0.1	3.62	0.262	7.37	7.51	120	7.3	4.68	0.268	1.83	1.77	0.046	11.2
45	PAE,1.0;sugar beet pectin,0.4	3.74	0.141	7.88	0.454	129	8.3	4.65	0.25	1.89	1.82	0.118	11.52
46	PAE,1.0;sugar beet pectin,1.0	4.08	0.214	8.85	0.251	117	10.3	5.04	0.137	2.06	1.89	0.106	11.96

[a]Pectin from citrus fruits.

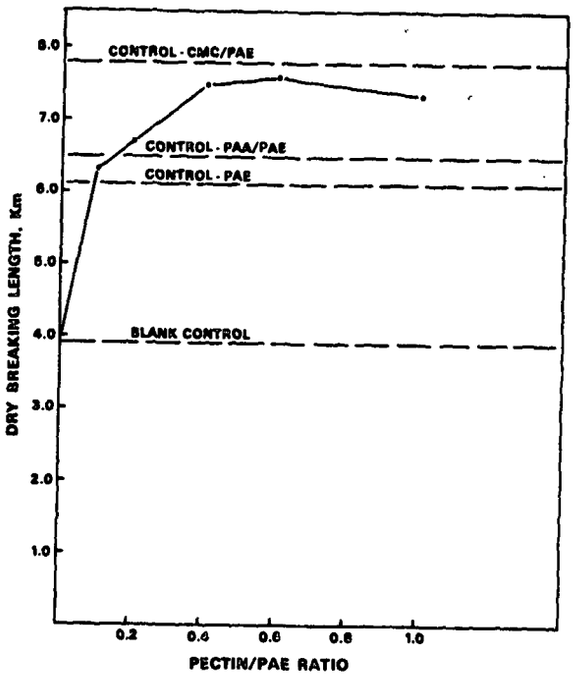


Figure 7. The effect of fruit pectin/PAE ratio on dry breaking length (49% yield softwood unbl. kraft - classified).

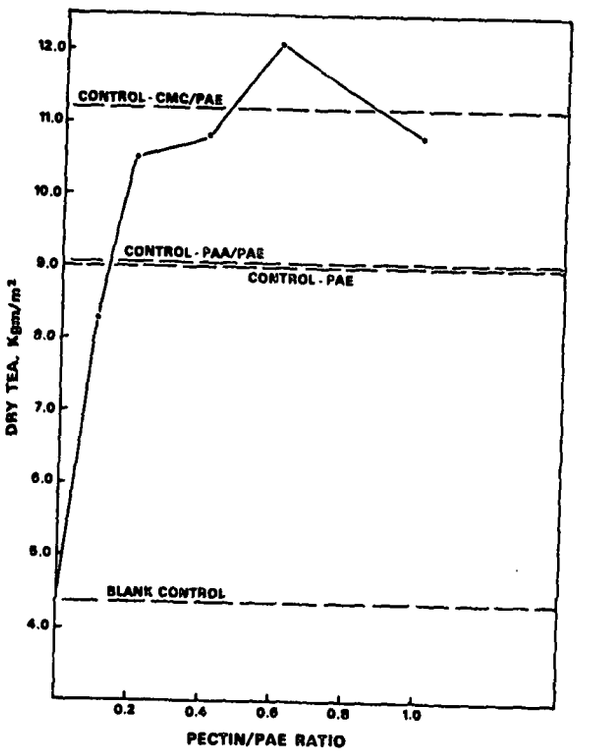


Figure 8. The effect of fruit pectin/PAE ratio on dry TEA (49% yield softwood unbl. kraft - classified).

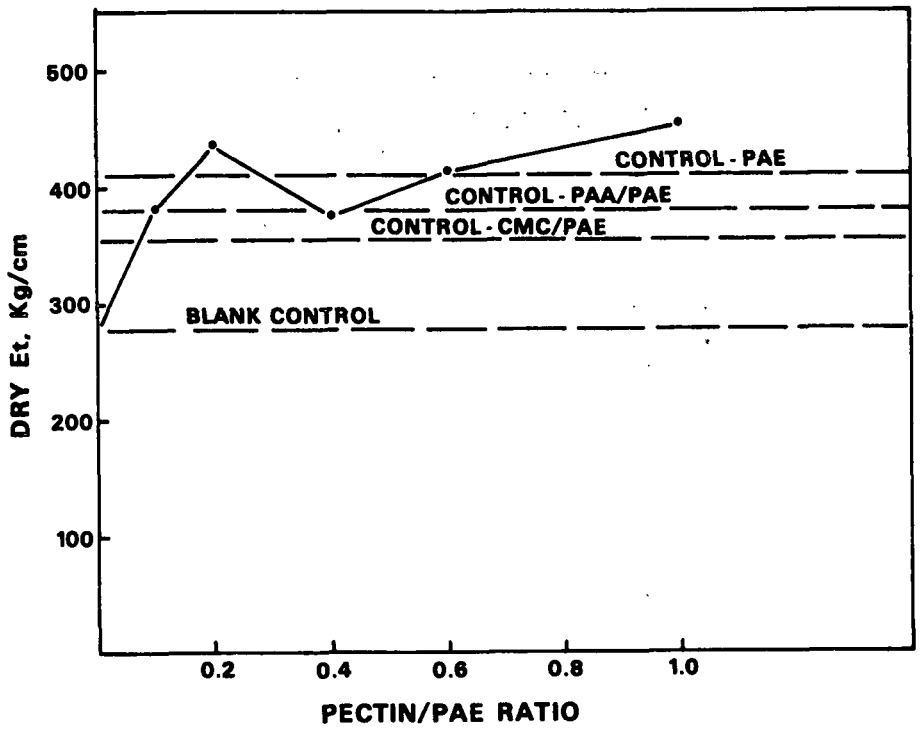


Figure 9. The effect of fruit pectin/PAE ratio on dry Et (49% yield softwood unbl. kraft - classified).

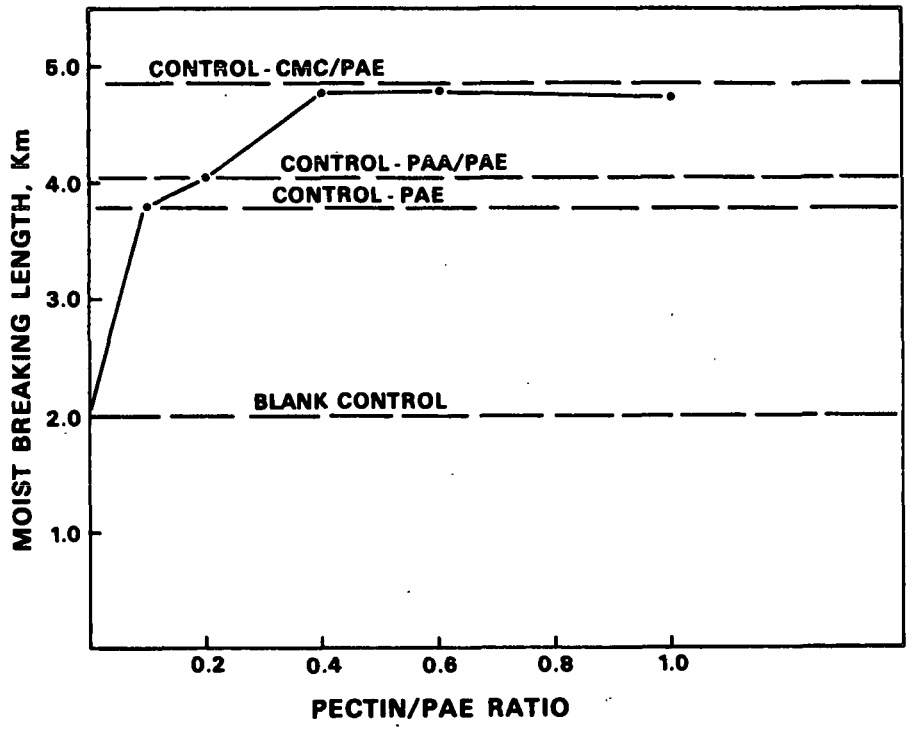


Figure 10. The effect of fruit pectin/PAE ratio on moist breaking length (49% yield softwood unbl. kraft - classified).

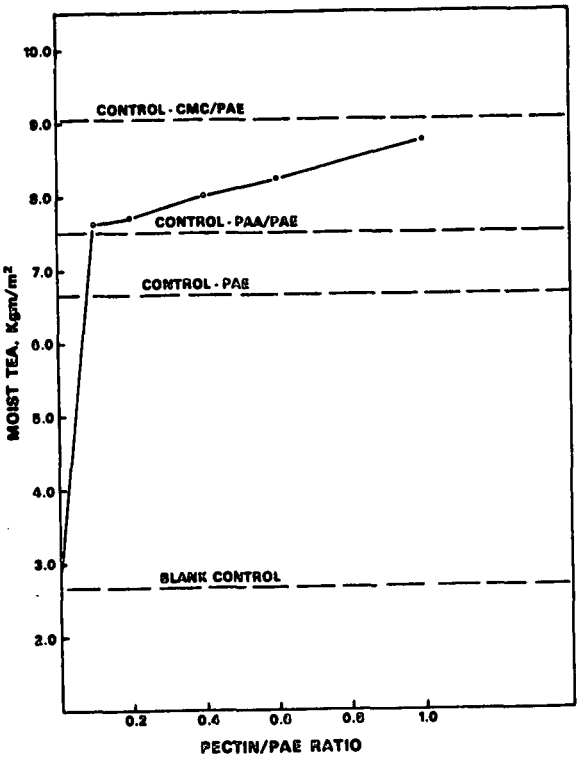


Figure 11. The effect of fruit pectin/PAE ratio on moist TEA (49% yield softwood unbl. kraft - classified).

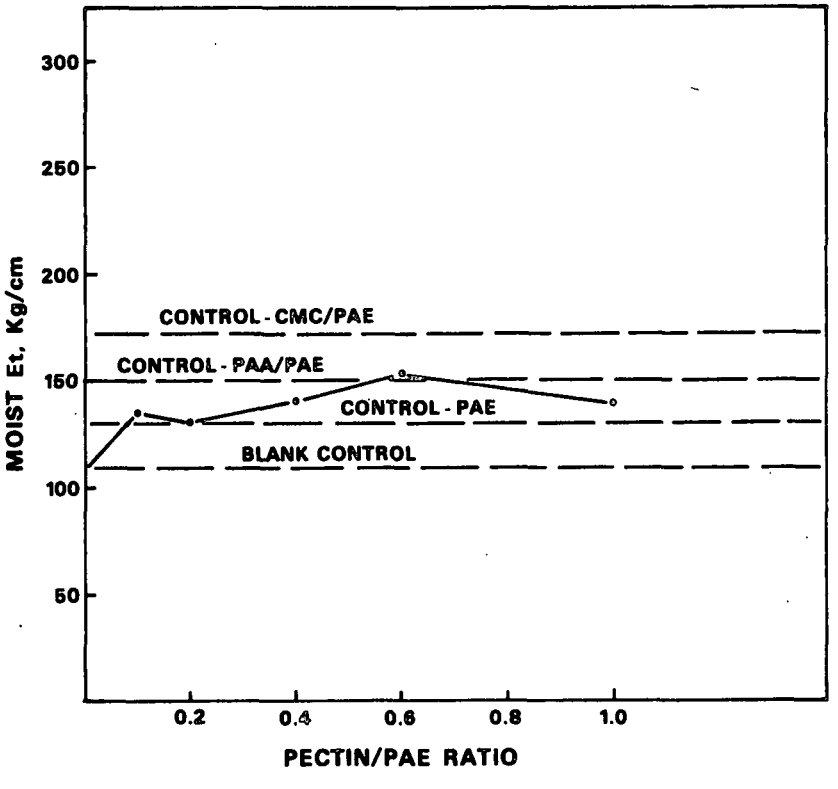


Figure 12. The effect of fruit pectin/PAE ratio on moist Et (49% yield softwood unbl. kraft - classified).

Results in Table 2 shows that the adsorption of pectins and related materials was low or zero. Further, selected pectins (Table 3) had little or no effect on strength properties. However, when combined with PAE (Table 4 and Figs. 7-12) the synergistic effect found with most previously tested anionic polymers was again evident. This applies to both the fruit and sugar beet pectins although the fruit pectin was more effective. In general, the fruit pectin/PAE combinations produced strength properties which equalled or exceeded CMC/PAE or PAA/PAE depending upon the polymer ratio and addition level. However, somewhat higher additions and/or pectin/PAE ratios were required to achieve these advantages and, considering the cost of pectins, it would not be feasible to pursue this approach at the present time.

It would appear from Table 4 that the use of alum in combination with pectin was of little value except at pH 4 where moist Et was 1.5 X that the untreated control. All other strength properties were markedly lower than those derived from the pectin/PAE combinations.

The effect of treated and untreated fines in a lightly-beaten softwood TMP was studied to assess the efficiency of bonding agents and the influence of fines in high yield pulps. The results are presented in Table 5 and the effect of adding isolated fines back to the long (classified) fiber fraction is shown in Figs. 13-15. The pulp was subjected to light beating to eliminate fiber bundles thereby producing a fines content of 30% (through 200 mesh). Figs. 13-15 show that addition of untreated fines to the long fiber fraction approached or equalled the whole pulp in dry and wet tensile and dry Et but failed to equal the controls in TEA and moist strength properties. Doubling the normal fines content from 30 to 60% greatly increased most strength properties but the highest moist Et in the absence of bonding agents was provided by the whole pulp control. Several other noteworthy effects are indicated in Table 5.

Table 5. The effect of fines and bonding agents on strength properties - softwood TMP[a].

Set No.	Description-Additives, % Based on Fiber or Fines	Basis Weight, g/m²	Thick-ness, µm	Apparent Density, g/cc	Dry Strength Properties: Breaking Length Km	SD	TEA Kgm/m²	SD	Et Kg/cm	SD	Stretch %	SD
46	Blank controls - whole pulp	63.7	184	0.346	3.24	0.106	2.43	0.301	222.0	22.5	1.85	0.142
47	Blank controls - classified pulp	62.5	264	0.236	1.28	0.062	0.697	0.101	97.7	4.87	1.38	0.105
48	Classified pulp + 5% of untreated fines	62.4	247	0.252	1.65	0.085	0.885	0.129	122.0	6.2	1.4	0.129
49	Classified pulp + 10% of untreated fines	63.0	237	0.266	2.03	0.048	1.27	0.089	144.0	4.3	1.59	0.058
50	Classified pulp + 20% of untreated fines	63.2	215	0.294	2.56	0.048	1.53	0.07	190.0	7.6	1.44	0.096
51	Classified pulp + 30% of untreated fines	62.8	195	0.322	3.13	0.097	1.93	0.268	226.0	15.5	1.52	0.16
52	Classified pulp + 60% of untreated fines	63.8	166	0.385	3.86	0.125	2.57	0.421	284.0	19.5	1.61	0.187
	Classified pulp + 30% of treated fines Treatments											
53	PAE, 1.5	62.5	198	0.316	3.28	0.074	2.42	0.252	222.0	10.9	1.81	0.131
54	PAE, 1.0; CMC, 0.4	63.6	199	0.319	3.31	0.096	2.61	0.174	216.0	19.4	1.88	0.078
55	PAE, 1.0; PAA, 0.2	63.4	196	0.324	2.98	0.146	2.17	0.377	211.0	14.8	1.74	0.175
56	PAE, 1.0; CMC, 0.4[b]	63.6	192	0.331	3.9	0.177	2.99	0.431	250.0	4.3	1.89	0.172
	Treated classified pulp + 30% of untreated fines Treatments											
57	PAE, 1.5	62.7	192	0.326	3.96	0.216	3.32	0.226	234.0	16.0	2.06	0.101
58	PAE, 1.0; CMC, 0.4	64.2	198	0.324	4.09	0.237	3.45	0.526	265.0	15.6	2.02	0.191
59	PAE, 1.0; PAA, 0.2	63.7	196	0.324	3.53	0.179	2.86	0.445	238.0	14.7	1.92	0.171
60	PAE, 1.0; CMC, 0.4[c]	63.6	186	0.341	4.44	0.154	3.85	0.526	268.0	9.2	2.1	0.203
	Treated classified pulp + 30% of treated fines Treatments											
61	PAE, 1.5	63.2	199	0.318	3.92	0.147	3.57	0.442	235.0	20.4	2.18	0.197
62	PAE, 1.0; CMC, 0.4	63.9	198	0.323	4.41	0.154	4.18	0.275	238.0	12.7	2.28	0.104
63	PAE, 1.0; PAA, 0.2	63.7	192	0.331	3.89	0.207	3.32	0.572	242.0	19.6	2.02	0.22
64	Whole pulp, PAE, 1.5	65.5	202	0.324	3.22	0.106	2.8	0.199	202.0	7.9	2.07	0.095
65	Whole pulp, PAE, 1.0; CMC, 0.4	63.4	184	0.344	3.88	0.07	3.12	0.35	218.0	13.6	2.06	0.146
66	Whole pulp, PAE, 1.0; PAA, 0.2	62.8	188	0.334	3.41	0.136	2.55	0.347	194.0	15.2	2.01	0.2

[a]Hemlock; 30% of fines in whole pulp.
[b]Fines treated with CMC/PAE in an amount equivalent to that added to whole pulp.
[c]Classified fiber treated with CMC/PAE in an amount equivalent to that added to whole pulp.

Table 5. Continued...

Set No.	Description-Additives, % Based on Fiber or Fines	Moist Strength Properties: Breaking Length Km	Breaking Length SD	TEA Kgm/m²	TEA SD	Et Kg/cm	Et SD	Stretch %	Stretch SD	Moist Tensile Factor	Wet Breaking Length Km	Wet Breaking Length SD	Wet Tensile Factor
46	Blank controls - whole pulp	1.7	0.182	2.36	0.248	111.0	5.98	3.1	0.2	1.0	0.148	0.02	1.0
47	Blank controls - classified pulp	0.648	0.057	0.519	0.039	45.0	2.17	2.11	0.214	0.38	0.048	0.006	0.32
48	Classified pulp + 5% of untreated fines	0.803	0.051	0.763	0.082	52.8	3.1	2.25	0.138	0.47	0.071	0.003	0.48
49	Classified pulp + 10% of untreated fines	0.889	0.062	0.879	0.101	53.8	1.57	2.37	0.14	0.52	0.072	0.007	0.49
50	Classified pulp + 20% of untreated fines	1.15	0.101	1.38	0.18	69.9	4.88	2.74	0.177	0.68	0.109	0.006	0.74
51	Classified pulp + 30% of untreated fines	1.44	0.108	1.84	0.336	83.0	4.75	2.98	0.312	0.85	0.141	0.008	0.95
52	Classified pulp + 60% of untreated fines	1.74	0.047	2.95	0.339	92.5	5.68	3.86	0.429	1.02	0.15	0.0117	1.01
	Classified pulp + 30% of treated fines Treatments												
53	PAE, 1.5	2.02	0.158	3.06	0.383	73.2	2.28	3.97	0.213	1.2	0.962	0.007	6.5
54	PAE, 1.0;CMC, 0.4	1.9	0.056	2.85	0.108	75.8	2.97	3.82	0.197	1.11	0.826	0.026	5.6
55	PAE, 1.0;PAA, 0.2	1.81	0.11	2.8	0.272	75.2	2.96	3.83	0.177	1.06	0.65	0.02	4.4
56	PAE, 1.0;CMC, 0.4[b]	2.56	0.118	4.22	0.425	87.1	4.27	4.28	0.306	1.27	1.46	0.065	9.86
	Treated classified pulp + 30% of untreated fines Treatments												
57	PAE, 1.5	2.55	0.202	3.88	0.404	75.3	7.73	4.23	0.081	1.5	1.57	0.105	10.6
58	PAE, 1.0; CMC, 0.4	2.61	0.108	4.17	0.374	79.1	3.84	4.42	0.24	1.53	1.34	0.088	9.0
59	PAE, 1.0; PAA, 0.2	2.02	0.202	2.88	0.446	82.4	8.62	3.63	0.15	1.2	0.746	0.035	5.0
60	PAE, 1.0; CMC, 0.4[c]	2.88	0.122	4.79	0.474	94.0	4.08	4.37	0.274	1.69	1.63	0.054	11.0
	Treated classified pulp + 30% of treated fines Treatments												
61	PAE, 1.5	2.44	0.063	3.94	0.365	71.3	2.6	4.37	0.335	1.43	1.6	0.056	10.8
62	PAE, 1.0; CMC, 0.4	2.9	0.161	5.08	0.296	71.2	4.16	4.87	0.156	1.7	1.99	0.075	13.4
63	PAE, 1.0; PAA, 0.2	2.36	0.053	3.85	0.281	77.1	3.89	4.19	0.165	1.39	1.32	0.042	8.9
64	Whole pulp, PAE, 1.5	1.85	0.284	2.96	0.863	66.2	4.76	4.0	0.737	1.09	1.33	0.068	9.0
65	Whole pulp, PAE, 1.0; CMC, 0.4	2.79	0.116	4.44	0.328	124.0	48.2	4.08	0.144	1.64	1.57	0.103	10.6
66	Whole pulp, PAE, 1.0; PAA, 0.2	2.54	0.288	3.22	0.381	97.0	11.2	3.6	0.2	1.49	1.25	0.047	8.4

[a]Hemlock; 30% of fines in whole pulp.
[b]Fines treated with CMC/PAE in an amount equivalent to that added to whole pulp.
[c]Classified fiber treated with CMC/PAE in an amount equivalent to that added to whole pulp.

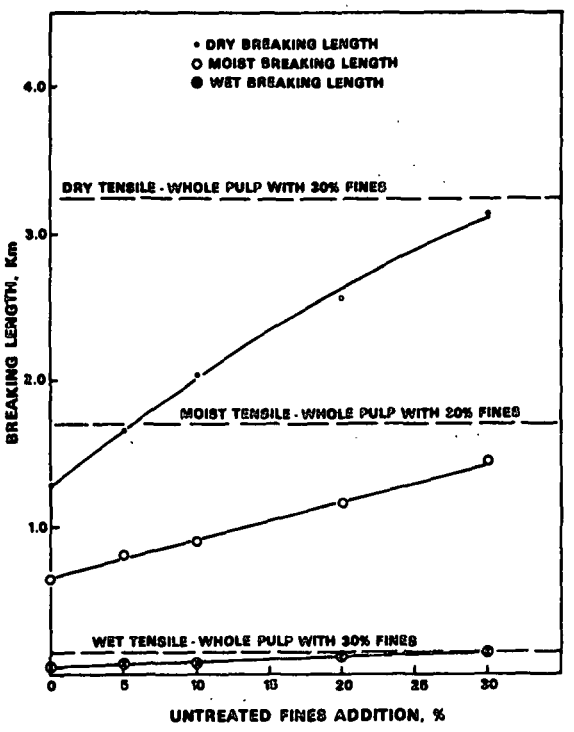


Figure 13. The effect of fines on tensile strength (Hemlock TMP).

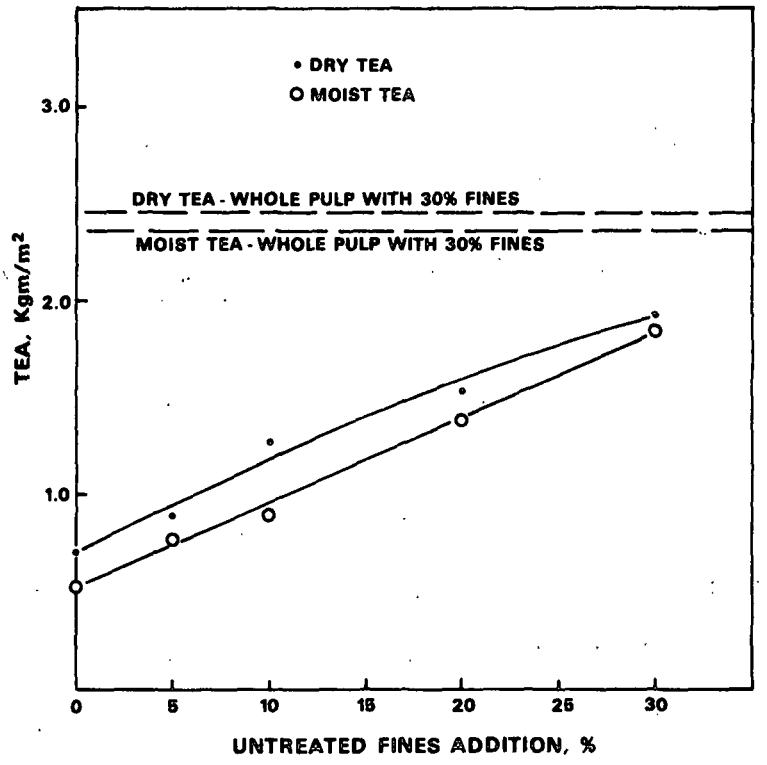


Figure 14. The effect of fines on TEA (Hemlock TMP).

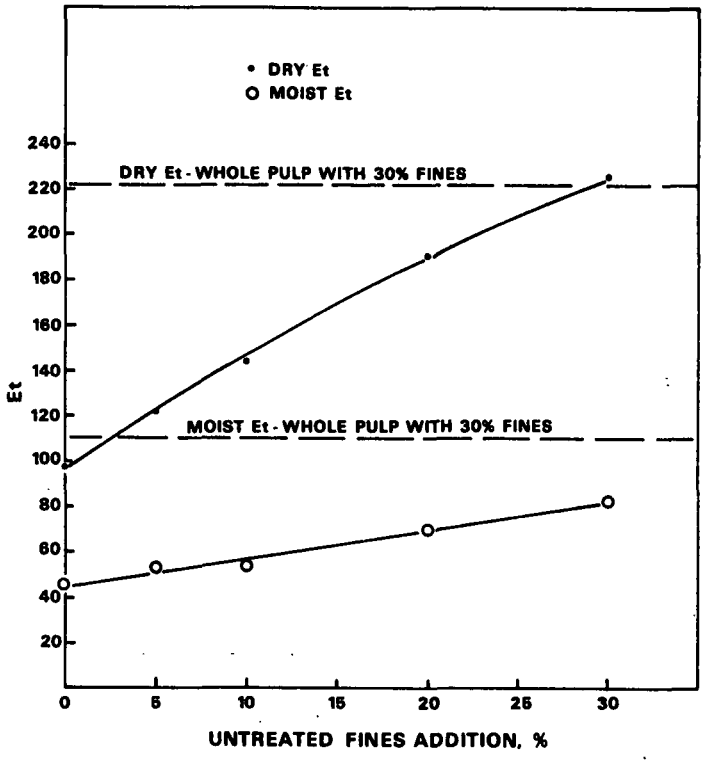


Figure 15. The effect of fines on Et (Hemlock TMP).

1. CMC/PAE proved generally superior to PAA/PAE.

2. Addition of CMC/PAE to the classified fiber was generally more effective than addition to the fines fraction treated separately.

3. With a few exceptions, combining treated classified fibers and fines to form a whole pulp produced higher dry, moist, and wet strength than adding the bonding agents directly to the original whole pulp. An exception was moist Et.

4. Treating the long fiber fraction with 1.4% of CMC/PAE was generally equivalent to, or superior to, the addition of 60% of untreated fines.

Conceivably the added polymers form bonded networks which trap fines in agglomerates which are poorly bonded to the whole fiber and are therefore less effective in forming a uniformly bonded structure. Thus addition to the long fiber fraction becomes more effective. Alternatively, a reduced level of covalent bonding may occur in the presence of fines due to the presence of interferring materials such as increased levels of lignin.

Recent evidence shows that the equilibrium moisture contents of whole pulps varies considerably in the presence of bonding agents at high relative humidity. This is probably due to variation in fines retention and it would be expected that moist strength properties would also vary under these conditions. Accordingly, it will be necessary to measure moisture content at high relative humidity for each set of handsheets prepared from whole pulps.

The use of diffuse reflectance FTIR analysis of polymer-treated papers was continued using handsheets from pulps differing in yield and wood source. In this case the additives were applied to the handsheet samples by immersing in solutions of the additives under controlled conditions followed ultimately by oven drying for 10 minutes at 105°C. The ratio of the 1740 ester band/1650 amide band was measured and the results are recorded in Table 6.

The fact that the A1740/A1650 ratios for the duopolymer systems were consistently higher than those of the 1% PAE controls supports earlier results (using model substrates) that ester formation and, hence, covalent bonds were formed. This applies to all pulps tested including the TMP where the presence of a "natural" ester was found in the untreated pulp controls.

Repulpability tests were carried out at pH 11.0-11.5 and 62°C on handsheets containing PAE, CMC/PAE, and PAA/PAE. The time of treatment and the Thwing formation test were used as a measure of relative repulpability. The pulp used for this purpose was a beaten, unclassified and unbleached softwood kraft pulp of 49% yield. The results of those tests which are presented in Table 7 and Fig. 16 indicate that papers containing the polymer combinations were repulpable to about the same extent as PAE alone yielding Thwing nos. comparable to those of the untreated controls.

Table 6. FTIR anlaysis of handsheets treated with polymer combinations.

Test No.	Pulp used in hand sheet preparations	Additives, % Solids	FTIR analysis; A1740(Ester)/ A1650(Amide)
	47-48% yield softwood unbl. kr., beaten and classified		
1		PAE,1.0	0.275
2		PAE,1.0;CMC, 0.4	0.436
3		PAE,1.0;PAA, 0.2	0.668
4		1:1 Starch:PAE,1.0;PAA,0.1	0.722
	49% yield softwood unbl. kr., beaten and classified		
5		PAE,1.0	0.268
6		PAE,1.0;CMC,0.4	0.610
7		PAE,1.0;PAA,0.2	0.416
8		1:1 Starch:PAE,1.0;PAA,0.1	0.417
	57% yield softwood unbl. kr., beaten and classified		
9		PAE,1.0	0.267
10		PAE,1.0;CMC,0.4	0.395
11		PAE,1.0;PAA,0.2	0.589
12		1:1 Starch:PAE,1.0;PAA,0.1	0.398
	88% yield softwood TMP[a] beaten 10 min, classified		
13		PAE,1.0	0.102
14		PAE,1.0;CMC,0.4	0.213
15		PAE,1.0;PAA,0.2	0.239
16		1:1 Starch:PAE,1.0;PAA,0.1	0.158
	88% yield softwood TMP[a] beaten 10 min, whole pulp		
17		PAE,1.0	0.173
18		PAE,1.0;CMC,0.4	0.316
19		PAE,1.0;PAA,0.2	0.329
20		1:1 Starch:PAE,1.0;PAA,0.1	0.342
	45-45% yield softwood unbl. kr., beaten, whole pulp		
21		PAE,1.0	0.192
22		PAE,1.0;CMC,0.4	0.329
23		PAE,1.0;PAA,0.2	0.329

[a]Ester band evident in blank controls, this may cause some interference in the FTIR analysis.

Table 7. Repulpability of treated papers from softwood unbleached kraft pulp, (49% yield, whole pulp; 370 ml CSF).

Set No.	Bonding Agents, % Based on Fiber	Treatment Time in Waring Blender,[a] Min.	Thwing Formation No.
67	None, Untreated Control	0	--
		1	20.7
		3	20.5
		5	20.8
		7	20.4
68	PAE, 1.5 (Ref. Control)	3	10.7
		5	17.2
		7	22.1
69	PAE, 1.0; CMC, 0.4	3	16.3
		5	20.8
		7	22.3
70	E, 1.0; PAA, 0.2	3	11.1
		5	21.6
		7	20.0

[a]pH 11.0-11.5; 62°C.

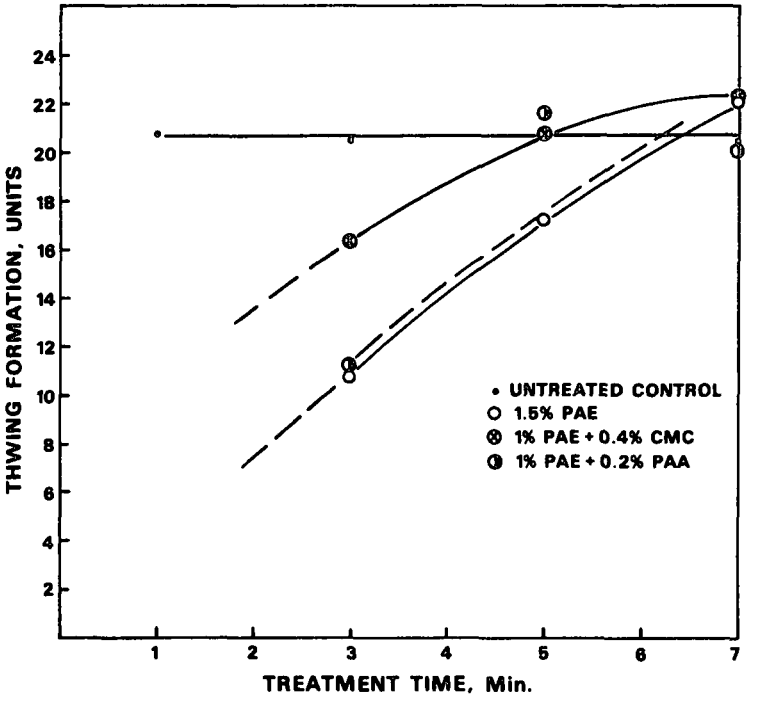


Figure 16. The effect of repulping time on sheet formation (49% yield southern pine unbl. kraft - whole pulp).

FUTURE WORK

(1) Further evaluation of new polymers in duopolymer systems including anionic and cationic components with the potential for ionic or covalent bonding. Particular emphasis in this and other units will be directed to means of improving moist strength properties.

(2) Extended additive use to include other high yield pulps such as a softwood chemimechanical.

(3) The role of fines in the use of chemical additives to establish how the additives and fines may interact to alter strength properties, particularly at high moisture levels.

(4) Expanded repulpability tests to include the strength properties of the recycled fiber.

(5) Continued study of chemical bonding mechanisms among those agents providing favorable strength properties.

STATUS REPORT

FUNDAMENTALS OF INTERNAL STRENGTH ENHANCEMENT

Project 3526

PART TWO: Fundamentals of Bonding.

INTRODUCTION

Van den Akker[1] has reviewed the parameters that are important to the strength of paper. Both experimentally and theoretically[2] tensile failure is found to depend on a) individual fiber strength and b) the extent and strength of fiber/fiber bonding. The present project will concentrate on improving the strength of the individual fiber/fiber bond.

It is apparent that, if we wish to strengthen the fiber/fiber bond by either mechanical or chemical means, we must know where failure occurs. Where is the weak link? Is it at the interface between the fibers or is it within the wall of one of the fibers? Only a few studies[3,5] have addressed this question. The results are mixed and appear to depend on the types of fibers used. Mohlin[3] measured the bond strength of never-dried springwood and summerwood kraft fibers bonded to cellophane. A scanning electron micrograph (SEM) of the area of bond failure shows a clean separation at the interface. Button[4] prepared lap joints (0° between the axes of the two fibers) of previously dried holocellulose. His SEM micrographs also showed failure to occur only in the interfacial region. In contrast Thorpe, et al.[5] found that the locus of failure depended upon the type of pulp. For a holocellulose fiber bonded at room temperature at a 90° crossing angle to a holocellulose shive, failure occurred at the interface in agreement with Button's results. Bonds formed at 110°C in the same geometry between a thermomechanical fiber and a thermo-mechanical shive, however, showed different behavior. They failed either in the lignin-rich layer between the fiber and the

shive, or in the S1 layer, or occasionally in the S2 layer. A statistical distribution was not given. When the bonds were formed at 210°C with the same TMP, lignin and hemicellulose flowed throughout the cell wall forming a continuum. A different pattern of failure resulted.

> "Failure in 45% of the 210°C bonds was due to fiber failure rather than bond failure, suggesting a very high bond strength. Bond failures usually resulted in a shearing across the entire cell wall thickness in the fiber or shive, with each retaining portions of the other's surface structure[5]."

Bond strengths of the 210°C bonds were about three times those of the 110°C bonds.

The data in the literature would appear to be too limited to draw any general conclusions. Variables were type of pulp, geometry, nature of substrate (or second fiber), and temperature of pressing. Part of the present study is designed to begin to fill in the gaps in our understanding of bonding failure loci.

RESEARCH RESULTS

In earlier work on this project we have shown that fiber/fiber bonds formed with apparently identical pressing procedures tended to fall into two discrete populations. Some had strengths greater than 0.5 g and others less than 0.2 g. In separate experiments we strained single fiber/fiber bonds to failure in the scanning electron microscope (SEM) and then examined the locus of failure. In some cases we could observe no difference between formerly bonded areas and adjoining unbonded areas. This would indicate the failure to be at the interface between the two fibers caused by a rupture of the hydrogen bonds. In yet other cases we observed various degrees of disruption of one or both of the fiber surfaces in the formerly bonded area.

Part of the cause of the different behavior may lie in different amounts of bonded area from sample to sample. To assess this area, we have chosen Page's vertical polarized illumination technique[6-8]. After mounting the bonded fiber pair on a Mylar tab, we photograph the bond area as viewed through crossed polaroids. Projection of the photograph (negative) provides a magnified image whose area can be determined planimetrically with a pressure sensitive board connected to an Apple II computer. The technique was found to give mixed results. In some cases the bonded area can be clearly distinguished. In others scattered light from portions of the fibers' lumens which are uncollapsed make the determination less certain.

The three measurements - bond strength, bond area, and locus of failure - were developed individually on single fiber/fiber bonded pairs. The next stage of the research is to perform all three measurements on the same fiber pair to determine the interrelations. During the past period the construction of the new fiber load elongation recorder (FLER II) was completed. This instrument is more sensitive than the earlier model and in addition can be used to test at constant rate of elongation as well as constant rate of loading. To date we have experienced difficulties in maintaining an intact bond during the procedure for mounting the sample in the instrument. We are currently developing new techniques for this procedure which will eliminate the problem.

Part of the objective of this project is to develop paper and board that is more tolerant to conditions of high humidity. To better assess the effects of moisture on stiffness, we have developed a non-destructive test of the bending modulus of a sample. The vibrating reed technique yields the elastic part of the complex dynamic modulus and can be related to results obtained by conventional stress-strain (Instron) or ultrasonic measurements. We have constructed

a system for maintaining constant or varying the relative humidity in the sample chamber at room temperature. This instrument will allow us to measure the change in bending modulus as a function of moisture content (relative humidity) on a single sample, thereby eliminating the inherent sample-to-sample variability.

FUTURE WORK

(1) Strength/bond area/locus of failure data will be obtained on fibers from a conventional yield unbleached softwood kraft pulp.

(2) Similar measurements will be made on this pulp treated with the additives found to be most effective in Part One of this project.

(3) The effects of pulp yield and refining will be similarly studied to obtain a better understanding of how these parameters affect individual fiber/fiber bond strength.

(4) The effects of moisture on the stiffness of samples generated in Part One of this project will be studied using the vibrating reed instrument.

LITERATURE CITED

1. Van den Akker, J. A., Tappi 53(3):388(1970).

2. Page, D. H., Tappi 52(4):674(1969).

3. Mohlin, U-B., Svensk Papperstid. 77(4):131(1974).

4. Button, A. F., Doctoral Dissertation. Appleton, Wisconsin. The Institute of Paper Chemistry, 1979.

5. Thorpe, J. L., Mark, R. E., Eusufzai, A. R. K., and Perkins, R. W. Tappi 59(5):96(1976).

6. Page, D. H., Paper Tech. 1:407(1960).

7. Page, D. H., and Tydeman, P. A., Paper Tech. 1:519(1960).

8. Page, D. H., Tydeman, P. A., and Hunt, M. In Bolam's Formation and Structure of Paper, Tech. Sec. BPBMA, London, Vol. I., p. 171(1962).

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3332

ON-LINE MEASUREMENT OF PAPER MECHANICAL PROPERTIES

October 22, 1985

PROJECT SUMMARY

Date: 9/10/85
Budget: $75,000
Period ends: 6/30/86
Project No.: 3332

PROJECT TITLE: ON-LINE MEASUREMENT OF PAPER MECHANICAL PROPERTIES

PROJECT STAFF: G. A. Baum, C. C. Habeger

PROGRAM GOAL:

Develop ways to measure and control manufacturing processes.

PROJECT OBJECTIVE:

To develop the capability to measure elastic parameters on a moving paper web. Current emphasis is on in-plane measurements on low basis weight papers and on out-of-plane measurements.

PROJECT RATIONALE, PREVIOUS ACTIVITY and PLANNED ACTIVITY FOR FISCAL 1985-86 are on the attached 1985-86 Project Form.

SUMMARY OF RESULTS LAST PERIOD: (October 1984 - March 1985)

1. A comprehensive report covering the work for FKBG (the Owens-Illinois-Valdosta sensor) has been written.

2. The DOE proposal concerned with on-machine measurements (both in-plane and out-of-plane) is now expected to be funded before June, 1985.

3. The automated in-plane laboratory system is completed except for a cover. It is discussed in the Project 3467 Status Report.

4. Equipment to measure mechanical properties as functions of temperature and moisture is under construction. This will be used for fundamental research and also used for obtaining calibration curves for on-machine sensors.

SUMMARY OF RESULTS THIS PERIOD: (April 1985 - September 1985)

1. The comprehensive report covering the work for FKBG (the Owens-Illinois Valdosta sensor) has been published, dated May 15, 1985.

2. A paper summarizing the results obtained in Valdosta was written for publication in Tappi. This is IPC Tehnical Paper No. 157, entitled "On-line measurement of paper mechanical properties", a copy of which is attached as Appendix I.

3. The DOE proposal concerned with in-plane and out-of-plane measurements is expected to be funded at the start of the next government fiscal year (October).

4. The automation of the measurements of out-of-plane elastic properties described in the Project 3467 report translates directly into this project, concerned at present with on-line measurements of ZD properties.

5. The improved transducer design, also described in the Project 3467 report, is also the key to the success of the on-line measurement of ZD properties.

6. The ultrasonic laboratory measurement system in the oven, also described earlier, will be useful in this project to determine appropriate moisture and temperature corrections to the on-machine measurements.

7. Work on the effects of refining and yield on ZD properties is continuing. Pulp samples have been prepared and refining has begun.

PROJECT TITLE: On-Line Measurement of Paper Mechanical Properties

PROJECT STAFF: G. A. Baum/C. C. Habeger

PRIMARY AREA OF INDUSTRY NEED: Properties related to end uses

PROGRAM AREA: Control of manufacturing processes

Date: 6/1/85
Budget: $75,000
Period ends: 6/30/86
Project No.: 3332
Approved by VP-R:

PROGRAM GOAL: Develop ways to measure and control manufacturing processes

PROJECT OBJECTIVE:

To develop the capability to measure elastic parameters on a moving paper web. Current emphasis is on in-plane measurements on low basis weight papers and on out-of-plane measurements.

PROJECT RATIONALE:

The ability to measure mechanical properties on the paper machine is valuable from several standpoints. It provides a potential means for control of process variables. It also provides a non-destructive way to assess product quality on a continuous basis, since certain mechanical properties are correlated with common end use paper specifications.

RESULTS TO DATE:

Developed theory of ultrasound propagation in paper, and developed devices for measuring paper and board in-plane elastic parameters on-machine. Successfully tested devices in mill environments. Constructed and tested a version useful for light weight grades which is also self-calibrating. Most recently developed cross correlation technique for use with in-plane velocity measurements, and initiated work relating to on-line measurements of z-direction properties. Designed, built, and tested a robotic instrument for measuring in-plane velocities in paper.

PLANNED ACTIVITY FOR THE PERIOD:

We intend to continue studies to explore the possibility of making out-of-plane ultrasonic measurements on a moving paper web. We will develop high frequency, broad banded, and low impedance transducers for good acoustic coupling to paper in the z-direction. We plan to look at both ceramic and plastic piezoelectric transducer constructions. Hardware and software for a high speed data acquisition system will be designed and built. On-line caliper measurements techniques will be investigated to be used with the ZD measurement system.

POTENTIAL FUTURE ACTIVITIES:

A proposal has been submitted to the Department of Energy to investigate possible control strategies on the paper machine, and to develop a sensor to measure out-of-plane properties.

Status Report

ON-LINE MEASUREMENT OF PAPER MECHANICAL PROPERTIES

Project 3332

The main activity directly related to Project 3332 has been the construction of a controlled environment ultrasonic tester. This partially automated apparatus can measure ultrasonic velocities at variable humidity from room temperature to 100°C. The primary reason for building this equipment is to develop moisture-temperature corrections for on-line ultrasonic measurements. By studying the behavior of typical samples, we hope to empirically develop an efficient form for the correction formulae. Samples of grades to have on-line instrumentation could then be tested and the correction parameters calculated. The secondary reason for the variable environment apparatus is to allow fundamental studies of the effects of moisture and temperature on ultrasound in paper. Of particular interest, will be student work on the "mechano-sorptive" transient effect at ultrasonic frequencies.

Bender transducers, similar to those we built for the automated, in-plane system, are the active elements in this tester. They are mounted, through coroprene acoustic absorbers, to an open frame which is hinged to a plate. The plate is mounted on the side of the oven; so that, the hinge is near the top of the oven. The open frame is held to the plate with a light spring. A stepping motor drives an eccentric cam between the plate and the frame controlling the frame-plate spacing. The sample is mounted in a wire frame connected by a thin rod (through a hole in the top of the oven) to a digital balance. With the cam in open position, the sample is weighed. When the cam is closed, the transducers contact the sample, which is tested ultrasonically. It is necessary to place an infrared lamp just above the top of the oven to avoid condensation on the weighing rod. Thermocouples are mounted near the four edges of the sample.

They are part of a digital thermometer with a parallel interface. The balance and thermometer are interfaced to an Apple computer, which also controls the stepping motor.

The environmental chamber is a Blue M oven. After some redesign of its baffling, it was possible to maintain the temperature variability between the sheet edges to less than one degree. Preliminary testing on paper sample has given reasonable and repeatable results.

At present, we are starting to look at the velocity-moisture-temperature relation and we will soon begin writing the software to combine the moisture and temperature detection and the stepping motor control with the automated ultrasonic velocity calculation.

The transducer development described in the Project 3467 report has application to the on-line work as well. Hopefully, transducers of a similar design could be mounted in wheels for measurement of out-of-plane velocities on a moving web. The PVDF film loses sensitivity at high temperature; however, it should be possible to maintain sufficient signal.

To do on-line Z-direction measurement, we need a very fast analog-to-digital converter. Therefore, we have ordered a full 100 MHz analog-to-digital converter with a buffer memory and I.E.E.E. interface. The Hewlett-Packard oscilloscope used in the laboratory version is unacceptable on-line. It does its high speed A to D by using a fast sample-and-hold-circuit and analyzing multiple repetitive signals. At one signal per revolution, it would require a prohibitively long time to do the conversion on-line.

Appendix I

IPC Technical Paper Series

Number 157

On-line measurement of paper mechanical properties

C. C. Habeger and G. A. Baum
The Institute of Paper Chemistry, P.O. Box 1039, Appleton, Wis. 54912

ABSTRACT

A sensor which determines the elastic properties of paper during manufacture is described. The sensor actually measures ultrasound velocities which are related to the elastic properties and sheet density. Since elastic properties are sensitive to machine operating conditions, the sensor could be used to monitor the machine performance and provide feedback for process control. In many cases, strength properties correlate with elastic properties; therefore, the sensor is also a product quality monitor. The operating principles are explained and the results of a mill trial are presented.

Introduction

A previous publication (1) discussed the importance of monitoring paper mechanical properties during the manufacturing process and described an ultrasonic sensor capable of making such measurements. This paper describes a new version of the sensor which was installed on an Owens-Illinois linerboard machine in Valdosta, GA, in December, 1982, and the results that were obtained over a two-year time period. This research was supported by the Fourdrinier Kraft Board Group (FKBG) of the American Paper Institute. The sensor developed under this project is therefore referred to in the following sections as the FKBG sensor.

The original sensor (1) and the FKBG sensor both use transducers mounted in wheels which are driven by the web. The piezoelectric transducer in each wheel is resonant at 80 kHz, a value well above most machine noise but below the point where the plate waves in paper become dispersive (2). The transducers are coupled to the rim of the wheel through an aluminum "button" which is mechanically isolated from the rest of the wheel. One wheel serves as a transmitter; two others act as receivers. One receiver is displaced in the machine direction (MD) from the transmitter, while the other is displaced in the cross-machine direction (CD). The transducer wheels are mechanically isolated from each other and from the supporting member (and thus from mill vibrations). The transducer wheels are synchronized so that the buttons contact the web at approximately the same time.

When the transducers contact the paper, the transmitter is excited with a burst of sine waves, and the vibrating transducer creates a mechanical disturbance in the moving paper web. This disturbance propagates away from the transmitter in all directions. The receiver wheels in the MD and CD directions

detect the disturbance after some time has elapsed. The "time-of-flight" of the mechanical disturbance is measured and, using the separation distance of the wheels, the velocities of sound in the MD and CD of the paper web are calculated. The time-of-flight approach was used, rather than a continuous wave method, to avoid undesirable interferences in the received signals due to waves reflected from the edges of the web, between the wheels, and from rolls.

This basic description applies to either sensor. Significant improvements have been made in the FKBG sensor, however, in signal analysis techniques, transducer design and ruggedness, wheel position detection, and synchronization of the transmitter and receiver wheels for maximum signal output. The major difference between the FKBG system and the earlier version is the way in which the transit times are measured. In the original system the time-of-flight was recorded when the voltage of the received signal exceeded a set threshold level. Unfortunately, this technique was too sensitive to extraneous noise and a more sophisticated approach was needed. The operation of the FKBG sensor is discussed below.

The FKBG Sensor

The sensor mounted at the dry end of the paper machine is shown in Fig. 1. Figure 2 is a schematic of the FKBG sensor and support electronics for CD measurements. The magnetic Hall effect position detector pulses just before the transducer buttons contact the web. Using a phase lock loop circuit, a second pulse is produced after an electronically adjustable angle of wheel rotation. This pulse triggers a signal generator. A 400-volt pulse of sine waves is delivered to the transmitter wheel, and a mechanical disturbance is created in the paper. After about 100 μsec, the disturbance is detected by a receiver

wheel in the cross machine (or machine) direction of the web. A preamplifier in each receiver wheel amplifies the signal immediately after it is received. Power to the preamplifier and the signal transmitted out of the wheel are passed through the same mercury slip-rings. The received signals are then passed through isolation transformers to reduce noise generated by ground loops. Line drivers transfer the signals over the 100 feet of 50-ohm coaxial cable between the sensor head and the central electronics cabinet.

[Figure 1 and 2 here]

The signals are digitized at a rate of five samples per microsecond by a Biomation Model 2805 high-speed waveform recorder. It is triggered at the same time as the transmitter and records the following 410 microseconds of received signal. After the analog-to-digital conversion, the digitized data is transferred to the microcomputer over a parallel interface. This transfer is made in less than one revolution of the wheel so that the Biomation is ready to accept a new signal at the next firing of the transmitter. In order to reduce noise and average out web variability, an adjustable number (1 to 100) of consecutive digitized signals are summed to produce a composite signal. Figure 3 shows a typical composite signal.

[Figure 3 here]

Each digitized receiver response has an initial portion, greater than 50 μsec, that contains only noise. This flat section (or baseline in Fig. 3) is analyzed to establish a zero signal level and a noise threshold. The software steps through the rest of the digitized composite signal, finds excursions from the baseline significantly greater than the noise threshold, and locates the descending crossing times (the times at which the waveform crosses zero

moving downward, indicated by the solid circles). The transit times in the paper are determined from a zero crossing time. A calibration procedure, utilizing manual changes in the wheel separation distances, allows the nonpaper delay times to be calculated. By subtracting the nonpaper delay from the transit time, the time-of-flight in the paper is determined. The separation distances between the transmitter and receiver wheels are known, so the velocity of sound in the web is simply the ratio of distance to transit time. MD and CD measurements are made alternately. The microcomputer software, which is written in both Basic and an assembly language, is stored in EPROMs so that the program is not lost during power failure or shutdown.

The measured velocities are displayed on a CRT in the electronics console, printed out, and sent to an analog output for communication with other systems. The FKBG sensor measures a longitudinal velocity, V_L, in the machine direction of the web and a shear velocity, V_S, in the cross-machine direction of the web. These are related to the elastic parameters by the following equations:

$$V_L = [(E_1/\rho)(1 - \nu_{12}\nu_{21})]^{1/2} \quad \text{and} \tag{1}$$

$$V_S = [G_{66}/\rho]^{1/2}, \tag{2}$$

where ρ is the density, E_1 is Young's modulus in the paper machine direction*, G_{66} is the shear modulus in the 1-2 plane, and ν_{12} and ν_{21} are the two Poisson ratios in the 1-2 plane. In paper the product of the Poisson ratios is typically small [about 0.07, see Ref. (3)] so that it is convenient to rewrite Eq. (1) as $V_L \approx [E_1/\rho]^{1/2}$. The square of the measured sound velocities are thus mass

*Paper is usually described as an orthotropic elastic material (2). The machine direction is defined as the 1 (or x) direction, the cross machine direction as the 2 (or y) direction, and the thickness direction as the 3 (or z) direction.

specific elastic moduli. Any furnish or machine operating variable which affects the density or elastic properties of the paper will change the measured velocities.

Paper is a viscoelastic material and its mechanical properties are sensitive to temperature and moisture content. Therefore, to use the measured sound velocities to predict product quality it is necessary to take these factors into consideration. Based on experiments performed at The Institute of Paper Chemistry on mill samples, correction formulae were developed for moisture content and temperature. These formulae were linear within the ranges of values experienced in the mill. The corrections would differ with furnish, but were not very grade sensitive. The sound velocities measured with the FKBG sensor were corrected to a moisture content of 7% and a temperature of 25°C. The temperature and moisture content values were available from the Measurex process control equipment in the mill. These corrections were made in the Measurex process control computer and displayed on their color CRT display.

The Measurex CRT display is shown in Fig. 4. The main title "STRENGTH" is misleading since most entries are elastic parameters rather than strength parameters. The top line gives the company initials, mill location, machine number, the grade currently being manufactured, the date, and time of day. The bottom of the display gives the slice number (position across the width of the paper machine) at which the FKBG sensor is located, and the values of basis weight (lb per 1000 ft^2), web temperature (°F), and web moisture content (%) at that location. The last two values are used to correct the measured specific stiffnesses to constant temperature and moisture. They are measured by the Measurex scanner (see Fig. 1) and are actually a weighted average of a number of CD scans. They are updated approximately every two minutes.

[Figure 4 here]

The variables in the NOW column are updated about every 45 seconds. The top two values are the specific elastic stiffness in the MD ($E_l \rho \approx V_L^2$) and the specific shear stiffness ($G_{66}/\rho = V_s^2$), both corrected for temperature and moisture. MD EXT STIFF and SHEAR STIFF are obtained by multiplying the first two entries, respectively, by the basis weight. The CD EXT STIFF is the extensional stiffness in the cross direction and is computed from the MD extensional stiffness and the shear stiffness using an empirical relationship that applies to most Fourdrinier papers (3). Paper squareness, SQUARENESS, is a measure of the anisotropy in the plane of the paper and is the ratio of MD to CD extensional stiffnesses. RING CRUSH, MULLEN, and STFI COMPRS are tests of paper strength commonly measured on linerboard grades. The displayed values are predicted from the extensional and shear elastic stiffness values. The prediction algorithm was derived from tests conducted at IPC on mill samples. The average, AVG, and two standard deviation spread, SPREAD(2S), give the average and two sigma spread of the measured values beginning at the start of the construction of the current reel. Like the NOW column, these values are updated every 45 seconds. During reel turn-ups the Measurex scanner is removed from the web; therefore, velocities cannot be corrected for the environment at the time of turn-up.

The values shown in Fig. 4 provide a continuous record of the quality of the paper being manufactured and give an immediate warning when a problem arises. This is important to the papermaker, since, without an indication of mechanical integrity, a large quantity of substandard material can be produced before a problem is detected from tests taken at the end of the reel. The

sensor can also be used to "fine-tune" the paper machine to produce a product of more uniform quality and/or optimum specifications.

Test results

In order to study the response of the FKBG sensor to machine operating variables, the paper machine variables were changed one at a time. The variables studied were wet pressing pressure, stock consistency to the headbox, refining level, rush-drag ratio (jet-speed to wire-speed), wet pressing pressure, and wet straining in the draws. In all instances the measured elastic properties behaved as expected from laboratory studies, confirming that the sensor is capable of monitoring paper quality. The results, obtained from trend plots, are shown in Fig. 5-9.

[Figures 5-9 here]

Figure 5 shows the results of the change in the wet pressing pressure. The second wet press was unloaded at 10:20. The decrease in pressing pressure produced a drop in the specific extensional stiffness, the shear stiffness, and the predicted CD ring crush, all as expected. When the pressing pressure was returned to normal, the values returned to their previous levels.

As shown in Fig. 6, the rush-drag ratio was reduced in two separate steps and later returned to normal in one step. Decreasing rush-drag causes a smaller fiber orientation preference for the mechanical direction. Notice that there were no significant changes in shear velocity as a result of the rush-drag alterations. This is as expected, since the shear modulus is relatively insensitive to fiber alignment. However, the MD longitudinal velocity, as anticipated, decreased with lower rush-drag ratio, since less fiber alignment in the

MD decreases the MD modulus. This is particularly evident in the abrupt changes in MD longitudinal velocity occurring about one minute after the 9:01 and 9:20 changes. Since reel 6 turned up at a low rush-drag setting and reel 7 at a normal one, these effects could be checked by laboratory tests on the grab samples. The laboratory MD longitudinal velocity at reel 6 was 8% below the daily average of the grab samples. The corresponding number for reel 7 was 1% below average. The ratio of MD to CD longitudinal velocities squared is 20% below average for reel 6 and 5% over average for reel 7.

Changes in refining level were made by varying the current to the refiners. The sensor outputs were not very sensitive to these changes made in the refiner current. The only event that was related to the refining changes was a drop in both velocity signals about six minutes after a 20% decrease in refiner current (see Fig. 7). The lack of a strong response is attributed to the small effect of these refiner current changes on the paper properties. This interpretation is supported by the laboratory results which showed little variation in end-of-reel grab samples taken during the refining test. Also, O.I. personnel made hourly checks of pulp freenesses, and the 11:00 values (which should be high) are not significantly different than the daily average.

Figure 8 presents some of the trend plot results for changes in wet straining. The results of doubling and then restoring to normal the strain in the draw between the second press and the dryer section are shown. As expected, the MD longitudinal velocity responded abruptly to the change in draws about 30 seconds after initiation. Increased wet-straining produces a stiffer sheet in the MD. The effects on the shear velocity are not as pronounced, but shear velocity does appear to correlate positively with tension in the draws for this

on-line test. There were no reel turn-ups at the abnormal settings of the draws; therefore it was not possible to investigate the effects by testing grab samples.

The consistency of the stock to the wire was changed by adjusting the turbine speed. A decrease in turbine speed caused an increase in consistency. Figure 9 records the changes due to three successive reductions in the turbine speed. The behavior of V_{MD}^2 and V_S^2 during this time was to decrease with decreasing turbine speed but then to recover somewhat after 6 or 7 minutes. Apparently, some other machine variable was being adjusted which tended to compensate for the consistency changes and bring the sheet properties back toward their usual values. Reel 16 turned up at about 13:31, while the turbine speed was about 7% below normal. The grab sample from this reel had V_{MD}^2 about 6% below normal, consistent with the trend plots in Fig. 9.

In summary, the on-line sensor was capable of following the changes in properties due to the machine variables studied. In each case the changes were in the directions predicted by laboratory experiments. Most of the changes in machine variables were modest; that is, the machine operator selected a range where he knew he could still make paper. The concomitant changes in the measured elastic stiffnesses (or strengths predicted from them) are thus not much larger than the random variations in the sheet. This is true, even though each on-line sensor reading was an average of 50 separate tests taken about one foot apart. We think that these large, random, variations of mechanical properties make it impossible to judge the quality of an entire reel with traditional mechanical tests on grab samples at reel turn-ups. A monitor that can measure mechanical integrity over the full length of paper on the reel is necessary.

Paper mechanical properties can vary considerably across the width of the paper machine, even though the basis weight and moisture content profiles are uniform. Figure 10 shows a CD profile of about one-fourth of the width of the web on the backside of the paper machine, obtained by scanning the sensor across the web. The decrease in mechanical properties near the edge of the sheet results in a bell-shaped distribution in properties across the full width of the machine. This behavior usually can be traced to a nonuniform shrinkage of the paper web in the CD. Such measurements suggest that the sensor will be useful for monitoring the CD properties of the web, and eventually lead to ways to control them.

[Figure 10 here]

Conclusions

The on-machine ultrasonic sensor successfully measures ultrasound velocities and thus the specific elastic properties of the moving paper web. The sensor is valuable as a product quality monitor and as a process control sensor. The latter application requires that suitable means be found for controlling MD and CD paper machine variables. The device is useful now for tuning the paper machine and providing an indication in real time of the quality of the paper being manufactured. It has been licensed to two process control equipment manufacturers, Accuray and Measurex, and the first prototype units are expected to be available by the summer of 1985.

Literature cited

1. Baum, G. A., and Habeger, C. C. "On-line measurement of paper mechanical properties", Tappi 63(7): 63(1980).

2. Habeger, C. C., Mann, R. W., and Baum, G. A. "Ultrasonic plate waves in paper", Ultrasonics 17(2): 57(1979).

3. Baum, G. A., Brennan, D. C., and Habeger, C. C., "Orthotropic elastic constants of paper", Tappi 64(8): 97(1981).

Acknowledgments

The development of the on-line sensor for measuring paper mechanical properties is a result of the collective efforts of many people. The authors are especially indebted to Leon Straub, Dave Brennan, Will Wink, Jerry Kloth, Dale Young, and Bob Treleven, each who made significant contributions in one form or another, and to all the other Institute of Paper Chemistry staff who provided continued support and encouragement. Special thanks are also due Coke Stuart, Calvin Marshall, and especially Bernard Lenz, all of Owens-Illinois in Valdosta, as well as the operating personnel on the paper machine, who made our work there enjoyable and productive. Jim Walker and Rene Larive' of Consolidated Bathurst provided us with the basic transducer wheels and gave important counsel early in the project.

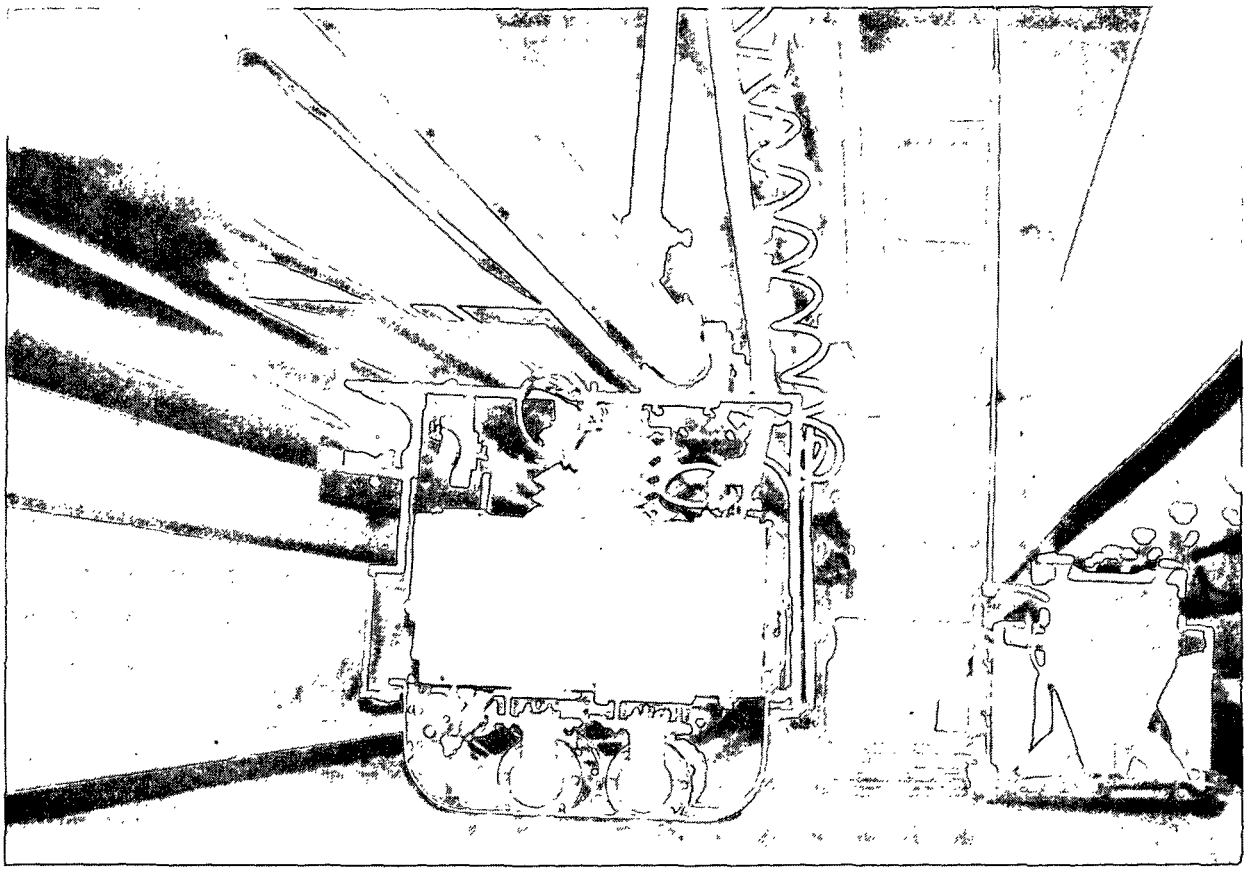


Figure 1. Ultrasonic sensor mounted next to a Measurex Scanner at dry end of paper machine.

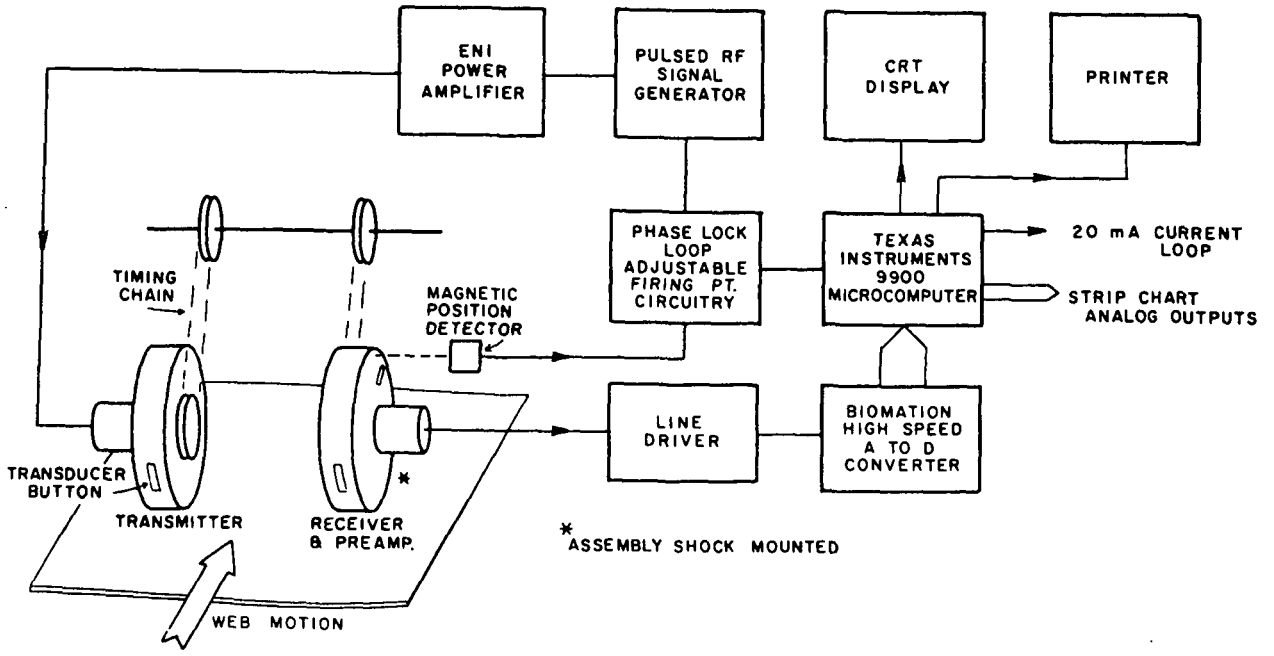
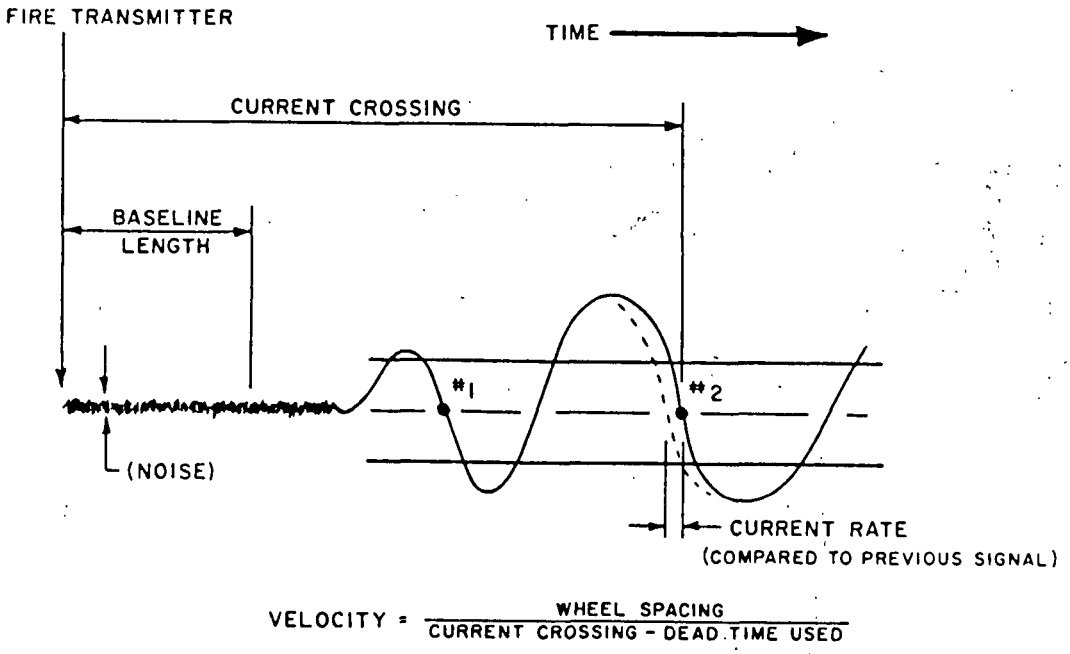


Figure 2. Block diagram of the ultrasonic stiffness gage. Wheel transducers shown are for cross machine direction measurements.



$$\text{VELOCITY} = \frac{\text{WHEEL SPACING}}{\text{CURRENT CROSSING} - \text{DEAD TIME USED}}$$

Figure 3. A typical averaged composite signal.

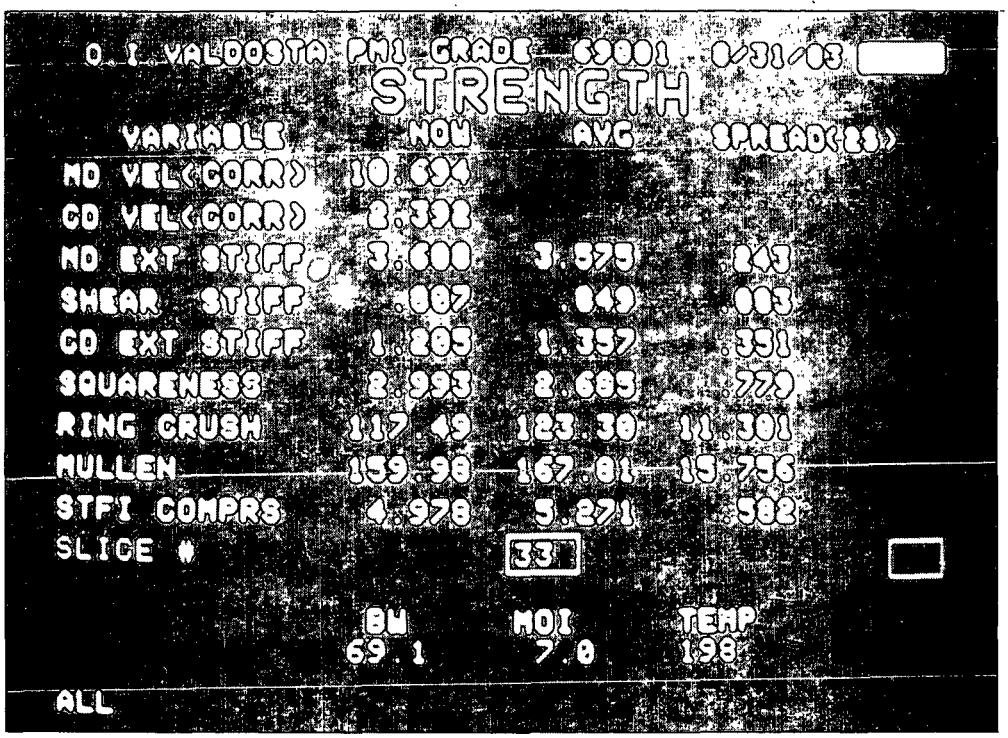


Figure 4. The Measurex CRT display.

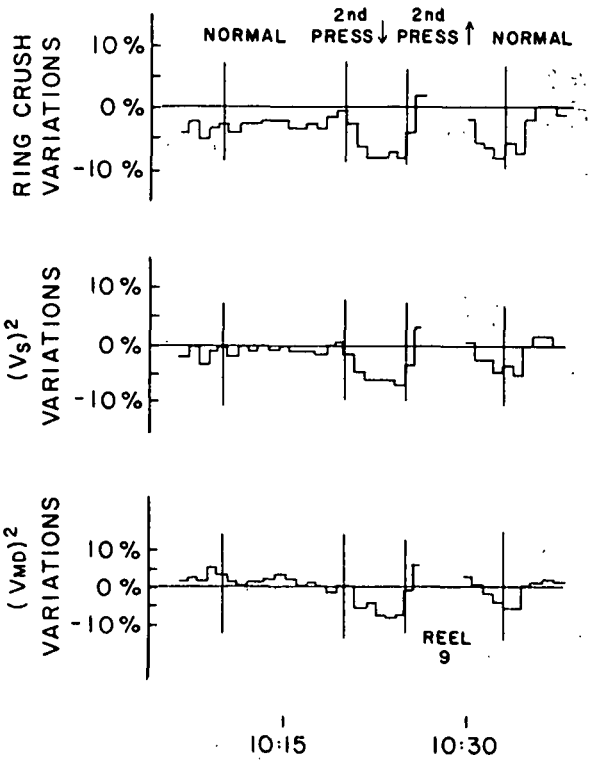


Figure 5. Wet pressure results.

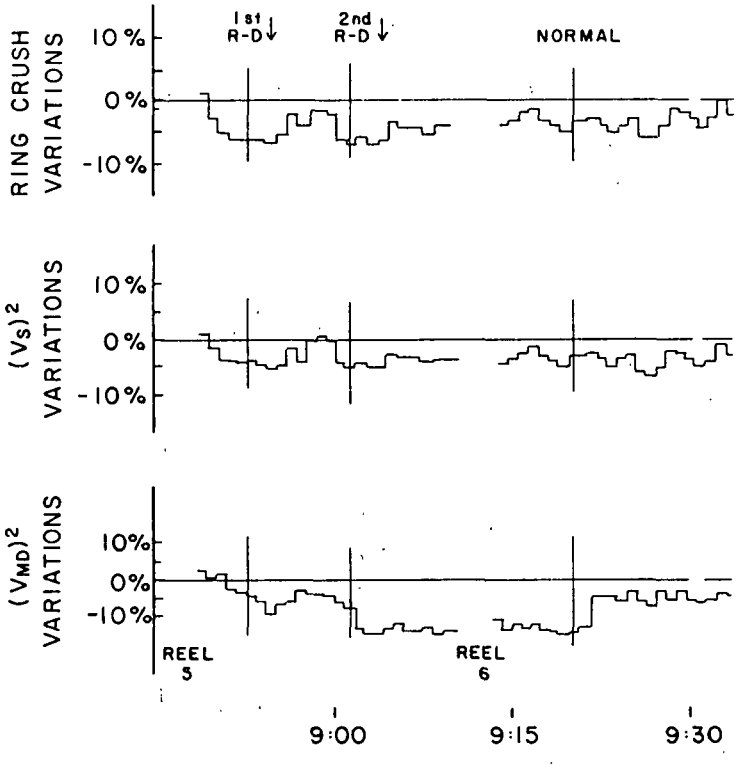


Figure 6. Rush-drag results.

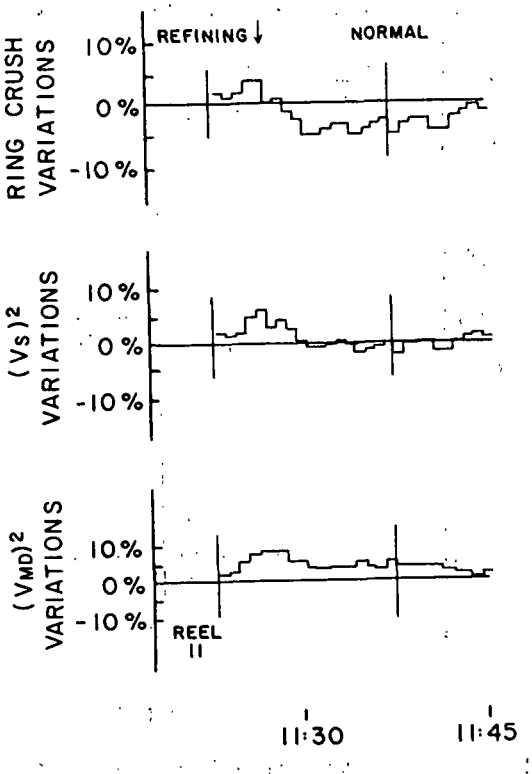


Figure 7. Refining results.

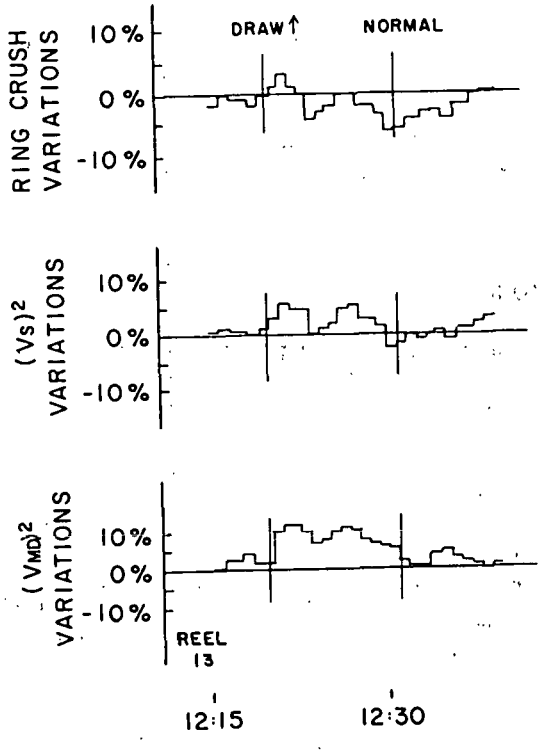


Figure 8. Wet straining results.

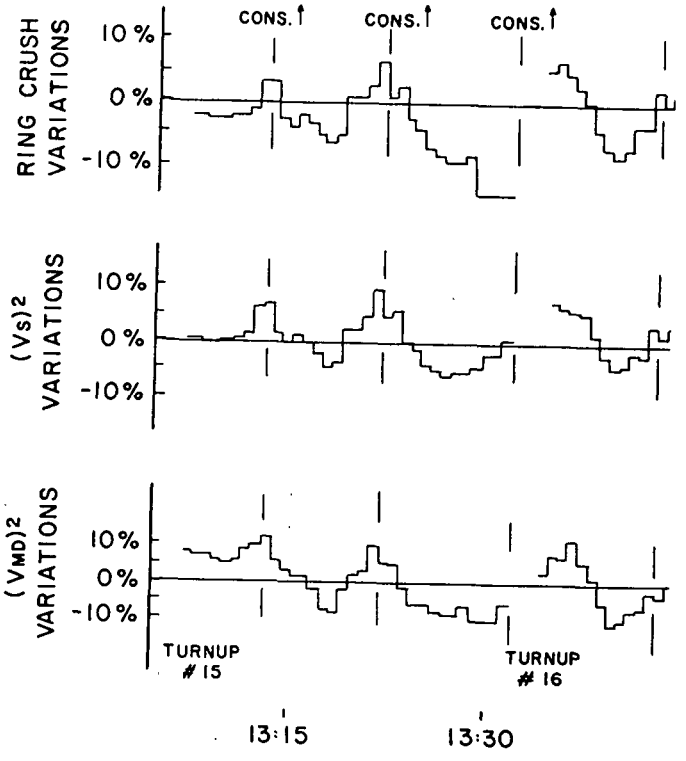


Figure 9. Consistency results.

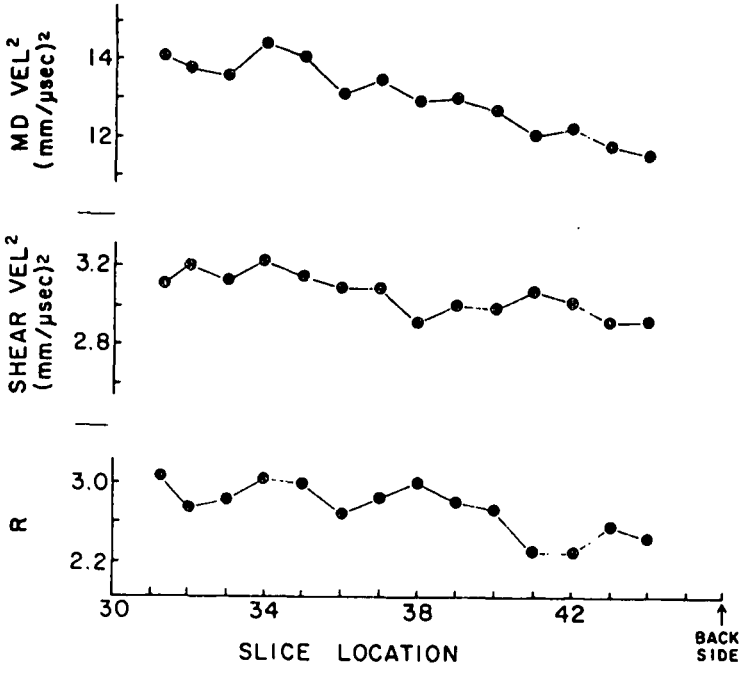


Figure 10. Slice location.

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

Status Report

to the

PAPER PROPERTIES AND USES

PROJECT ADVISORY COMMITTEE

Project 3566

STRONG, INTACT, HIGH YIELD FIBERS

October 22, 1985

PROJECT SUMMARY FORM

DATE: September 6, 1985

PROJECT NO. 3566: STRONG, INTACT, HIGH-YIELD FIBERS

PROJECT LEADERS: T. J. McDonough, S. Aziz

IPC Goal:

Significant increase in the yield of useful fibers.

OBJECTIVE:

Identify or develop methods of wood fiber separation which will allow the production of separated fibers having the same physical strength and geometrical form possessed when bound in the orignal wood matrix.

CURRENT FISCAL BUDGET: $170,000

SUMMARY OF RESULTS SINCE LAST REPORT:

Determinations of fiber strength in unpulped pine and spruce woods have been completed. Spruce and pine wood chips have been mechanically and chemimechanically treated in the Sprout-Waldron refiner and the Asplund mill. Single fiber and handsheet testing have been partially completed.

PLANNED ACTIVITY THROUGH FISCAL 1986:

Continued investigation of the effects of fiberization variables on fiber strength and integrity is expected to provide information on the fiberization mechanism and allow the identification of conditions that maximize fiber strength. The properties of artifically bonded paper made from these fibers will be compared with those of similar paper made from unbeaten kraft fibers. The feasibility of increasing fiber strength by selective wall component modification will be investigated.

FUTURE ACTIVITY:

Activity in the following areas will be planned and initiated: (a) correlation of wood properties and fiberization behavior, (b) alternative fiber separation methods, and (c) biological pretreatment of wood.

Status Report

STRONG, INTACT, HIGH-YIELD FIBERS

OBJECTIVES

The objective of this project is to identify or develop methods of wood fiber separation which will allow the production of separated fibers having the same physical strength and geometrical form as they possessed when bound in the original wood matrix. The current short term goals are to identify the factors governing retention of fiber strength and integrity during fiber separation and to develop methods for controlling them.

INTRODUCTION

Earlier work on this project showed that the major factors preventing state-of-the-art chemimechanical pulps from being as strong as kraft pulps are fiber strength and fiber conformability. We chose the first as the target of our initial efforts in a program to develop very strong high-yield pulps. There are two reasons for concentrating on fiber strength first. One is that we have prepared pulps with yields greater than 80% in which the strength of the sheet is limited by the strength of the fibers - increased densification beyond a certain point has no effect on sheet strength. The other is that control of fiber strength will probably be achieved by some means (chemical pretreatment or adjustment of refining conditions) that will also affect conformability. If the two problems are to be attacked separately, as seems highly desirable, solving the fiber strength problem first will define the starting material for solving the conformability problem; imparting conformability to fibers that have been treated to preserve or enhance their strength may be a different problem from imparting conformability to ordinary mechanical pulp fibers. Also, since the

manner in which the wood is fiberized affects fiber length retention, fiber conformability and energy consumption, it was decided to direct the project toward improving all aspects of the fiberization process, not just fiber strength retention. This reasoning established the goals of the current project, the initial emphasis being placed on the fiber strength aspect.

Our first report[1] described project goals and proposed activity, as well as collection of the wood to be used and initial results on its characterization. Early work on the development of a method for *in situ* measurement of wood fiber strength was also described. The second report[2] described completion of work on development of the method and its application to earlywood and latewood from well characterized locations within one of two loblolly pine trees collected for the project.

Since the work described in the second report was completed we have completed a similar characterization of spruce wood and have begun work on wood fiberization and characterization of the resulting coarse pulps, especially with regard to the strength of their fibers. Mechanical, thermomechanical and chemithermomechanical fiberization of both pine and spruce are being investigated. In addition, we have completed experiments designed to determine the effect of sulfonation *per se* on the strength of the fibers in southern pine earlywood, as well as its effect on fiber strength retention during subsequent mechanical and chemimechanical pulping.

Another component of our effort in recent months has been a preliminary assessment of the feasibility of initiating research at IPC on applications of biotechnology to high-yield pulping. This assessment, which included a literature survey, was prepared for us by a private consultant, Dr. J. V. Maxham. It is appended to this report.

ZERO-SPAN TESTING OF THIN WOOD SECTIONS

Disks taken from the butt log of a white spruce tree collected in northern Wisconsin were mapped, sawn and sectioned with a microtome to give thin sections measuring approximately 25 mm in the longitudinal direction, 20 mm in the tangential direction and 0.10-0.15 mm in the radial direction. Sections were cut from the earlywood, latewood and transition wood parts of each of three annual rings in each of 7 different radial locations in the disk. Each group of earlywood sections (from a given annual ring at a given location) consisted of about 10 specimens; fewer transition wood and latewood sections could be cut from any one annual ring, so these groups were somewhat smaller. All specimens were broken in a Pulmac zero-span tester, the load being applied in the longitudinal direction (parallel to the fiber axes). The fragments were retested to give a total of 6 measurements per section; these were averaged after discarding any obvious outliers and converted to breaking lengths with the aid of measurements of specimen dimensions and weight. The zero-span breaking lengths (ZSBL) for all specimens within a group were then averaged to give a single entry in Table 1 or 2.

Table 1. Spruce Earlywood ZSBL, km.

Location (Angle in Degrees)	Annual Ring 12	18	26
0	31		27
45	32		
90	33	37	35
180	32	32	36
225	30	30	30
270	32	32	33
Average		32	
Std. Dev.		2.5	

Table 2. Spruce Latewood ZSBL, km.

Location (Angle in Degrees)	Annual Ring 12	18	26
0	33		
90	44	44	42
180	49	52	45
225		46	
270	54	48	54
Average		46.4	
Std. Dev.		6.1	

These tables show that, as previously observed for pine wood, latewood fibers are stronger than earlywood fibers, even when the strengths are expressed as breaking lengths, which tends to remove the effect of wall thickness. (In calculating the breaking length, the breaking load is divided by the weight of the specimen.) This may be due to the smaller proportion of presumably weak middle lamella in latewood, larger proportion of S_2 wall layer, fewer and smaller pits in the fiber wall, or differences in fibril angle. Another point of similarity with the pine results is the absence of any marked systematic variation of the strength of a given fiber type with position across or around the tree.

Table 3 compares data for spruce and pine. The spruce fibers are about 50% stronger than their pine counterparts; this probably accounts in part for the higher tensile strength of papers made from spruce pulps.

Table 3. Summary: Wood ZSBL, km.

		Earlywood	Transition Wood	Latewood
Pine	Average	20		31
	Std. dev.	3		6
Spruce	Average	32	34	46
	Std. dev.	2	3	6

FIBER STRENGTH IN RMP AND CMP

As a first step toward understanding the effect of mechanical and chemimechanical separation on fiber strength we undertook a study[3] in which refiner mechanical pulp (RMP) and sulfonated chemimechanical pulp (SCMP) were prepared in the laboratory from characterized southern pine and the resulting fibers were subjected to single fiber load-elongation testing.

As a preliminary experiment, thin pine earlywood sections were sulfonated and tested to determine whether sulfonation itself has any effect on the strength of unseparated fibers, apart from any effect it may have on the mechanism and consequences of subsequent fiber separation in the refiner. Table 4 is typical of the data obtained and shows that the effect of sulfonation is to slightly increase section breaking length. The effect on the load bearing ability of the fiber is, however, negligible; the increase in breaking length is due to a slight yield decrease during sulfonation.

Table 4. Axial zero-span tensile strength of ultrathin wood sections, km.

	Disk 1		
Region	Before Sulfonation	After Sulfonation	Increase
1	22.1	26.2	4.1
2	23.6	24.6	1.0
3	22.7	26.2	3.5
4	24.3	24.6	0.3
5	24.7	24.8	0.1
6	22.4	24.4	2.0
7	26.4	23.4	-3.0
			+1.14

Two different samples of SCMP were prepared and compared with RMP. The first, designated SCMP1, was made under conditions known to give very strong pulps from spruce. Classification and testing of handsheets showed that this pulp, which had a yield of 98%, was actually poorer than RMP (Tables 5 and 6). Consequently, SCMP2 was prepared with NaOH added to the pretreatment liquor, in an effort to obtain improved properties. The resulting pulp had a yield of 85% and was higher in burst and tensile, but showed no tear improvement over RMP. Southern pine was not expected to perform nearly as well in the SCMP process as spruce, but this near total failure of the process to produce a better pulp than RMP was surprising.

Table 5. Bauer-McNett classification.

Pulp type	On 28-mesh, %	On 48-mesh, %	On 60-mesh, %	On 100-mesh, %	Through 100-mesh, %
RMP	16.8	24.9	10.9	9.5	37.9
SCMP1	5.9	32.2	18.4	13.8	29.7
SCMP2	10.4	45.0	8.8	18.1	17.7

Table 6. Handsheet properties.

Pulp Type	Pretreatment Yield, % o.d. wood	CS Freeness, mL	Density, g/cm^3	Burst index, $kPa \cdot m^2/g$	Tear index, $mN \cdot m^2/g$
RMP	--	110	0.26	0.54	3.84
SCMP1	98	235	0.28	0.33	2.01
SCMP2	85	325	0.33	0.63	2.97

Pulp Type	Extensional Stiffness, kN/m	Breaking Length, km	Tensile Index, Nm/g	Breaking Length, Zero-span, km
RMP	185.6	1.78	15.80	7.71
SCMP1	181.1	1.35	11.90	8.38
SCMP2	--	--	18.90	--

Fibers taken from the 28 and 48 mesh fractions of the above pulps were individually tested on the IPC load-elongation recorder. The results are laid out in Table 7. The SCMP fibers were similar to those of RMP in both breaking load and cross-sectional area, with the result that the breaking stresses of the two types of pulp were similar. This conclusion held true for both SCMP pulps. The three pulps were also similar with respect to modulus.

Table 7. Single fiber test results and their 95% confidence intervals.

Fraction (mesh size)	Pulp Type	No. of Fibers Tested	Load, g	C.S.A., um^2	Stress, kg/mm^2	El. Modulus, kg/mm^2	Strain, %
28	RMP	43	32 ± 4	582 ± 73	59 ± 8	1111 ± 274	7.2 ± 0.9
28	SCMP1	42	32 ± 4	534 ± 57	62 ± 7	1196 ± 209	6.8 ± 0.7
28	SCMP2	40	34 ± 4	588 ± 62	59 ± 4	1351 ± 161	7.8 ± 0.8
48	RMP	35	28 ± 4	557 ± 83	54 ± 6	1427 ± 200	7.0 ± 0.8
48	SCMP1	39	28 ± 5	522 ± 58	52 ± 6	1399 ± 174	6.8 ± 0.6
48	SCMP2	41	28 ± 4	591 ± 56	47 ± 4	1283 ± 148	6.3 ± 0.6
	Kraft[a] whole	127	15 ± 1	250 ± 9	62 ± 3	580 ± 30	18.3 ± 0.9

[a]Hardacker and Brezinski, Tappi 56(4):154(1973).

Fibers taken from the 48 mesh fraction were weaker than those from the 28 mesh fraction. One interpretation is that the same processes which result in fiber shortening also result in fiber weakening. Another is that fibers that become shortened during refining tend to be those that were initially weaker.

To allow a rough comparison of RMP and SCMP fiber strength with that of kraft, we retrieved from the literature data on a southern pine kraft pulp. These results, published in 1973 by Hardacker and Brezinski, are shown as the last row of entries in Table 7. The breaking stress of the kraft fibers was

about the same as we obtained for RMP and SCMP. However, closer examination of the data showed that it was obtained as the quotient of a 50% smaller breaking load and a 50% smaller cross-sectional area. The implication is that kraft fibers have only half the load bearing capacity, on an individual fiber basis, of high yield pulps such as the ones tested. This cannot be viewed as a firm conclusion until measurements are made on a kraft pulp prepared from the same wood supply that gave the high yield pulps.

Another interesting comparison can be made with the thin wood section data of Table 3. Pine earlywood and latewood sections had breaking lengths of 20 and 31 km, respectively. If it is assumed that a value of 25 represents an average for the mixture of earlywood and latewood in the chips used to make the pulps, this value may be compared with a fiber breaking length calculated from the single fiber data of Table 7. Approximating the fiber strengths in this table by a value of 60 and dividing by an assumed cell wall density of 1.5 gives a single fiber breaking length of 40. This gives rise to the seeming paradox that the pulp fibers are stronger than the fibers in the wood from which the pulp was made. A number of interpretations are possible. One is that the wood zero span test data do not truly reflect fiber strength because of stress concentration during the test. Another is that single fiber data are censored because the fibers tested were selected on the basis of their being long enough to easily mount in the testing jig. Longer fibers are likely to be stronger ones as discussed above with reference to Table 7. It seems likely that both factors come into play; all that can be concluded now is that at least some of the fibers in the high-yield pulps tested have strengths that are high in relation to the strength they once possessed as part of the original wood structure.

FIBERIZATION AND FIBER PROPERTIES

One of our objectives is to relate fiber properties to fiberization variables. Accordingly, we have begun to experiment with the preparation and evaluation of fibers separated under various conditions. A guiding principle in this work is that the experiments should be conducted in such a way as to allow the effects of the mechanical action that results in fiber separation to be separated from the effects of mechanical action applied to the fiber after separation. Accordingly, relatively mild conditions are used and fiberization is far from complete. The resulting material is separated into fibrous and non-fibrous fractions on a 0.006 inch cut flat screen.

The first experiments were done with southern pine chips in the Asplund mill. 300 Grams of chips were charged to the mill and fiberized for 2 minutes at a temperature of 120°C and a consistency of approximately 37%. Screening yielded 140.7 grams of accepts and 136.1 grams of rejects.

A property of primary concern was the zero-span strength of the accepts, but this proved difficult to measure because of the difficulty of forming handsheets from such coarse material. This was first circumvented by adding small amounts of well beaten sulfite pulp as a bonding agent, which gave the results shown in Fig. 1. In later experiments, other bonding additives were used to obtain the results shown in Fig. 2. In later experiments, improvements in technique, including the use of sailcloth as a forming medium, resulted in our being able to form sheets without bonding additives. These sheets had breaking lengths as high as 7.0 km. The conclusion was that the zero-span breaking length of sheets of the fibrous material was at least 7.0 km. For comparison with the wood section and single fiber data, this may be multiplied by 8/3 to correct for the random orientation of the fibers in the sheet, giving a value of

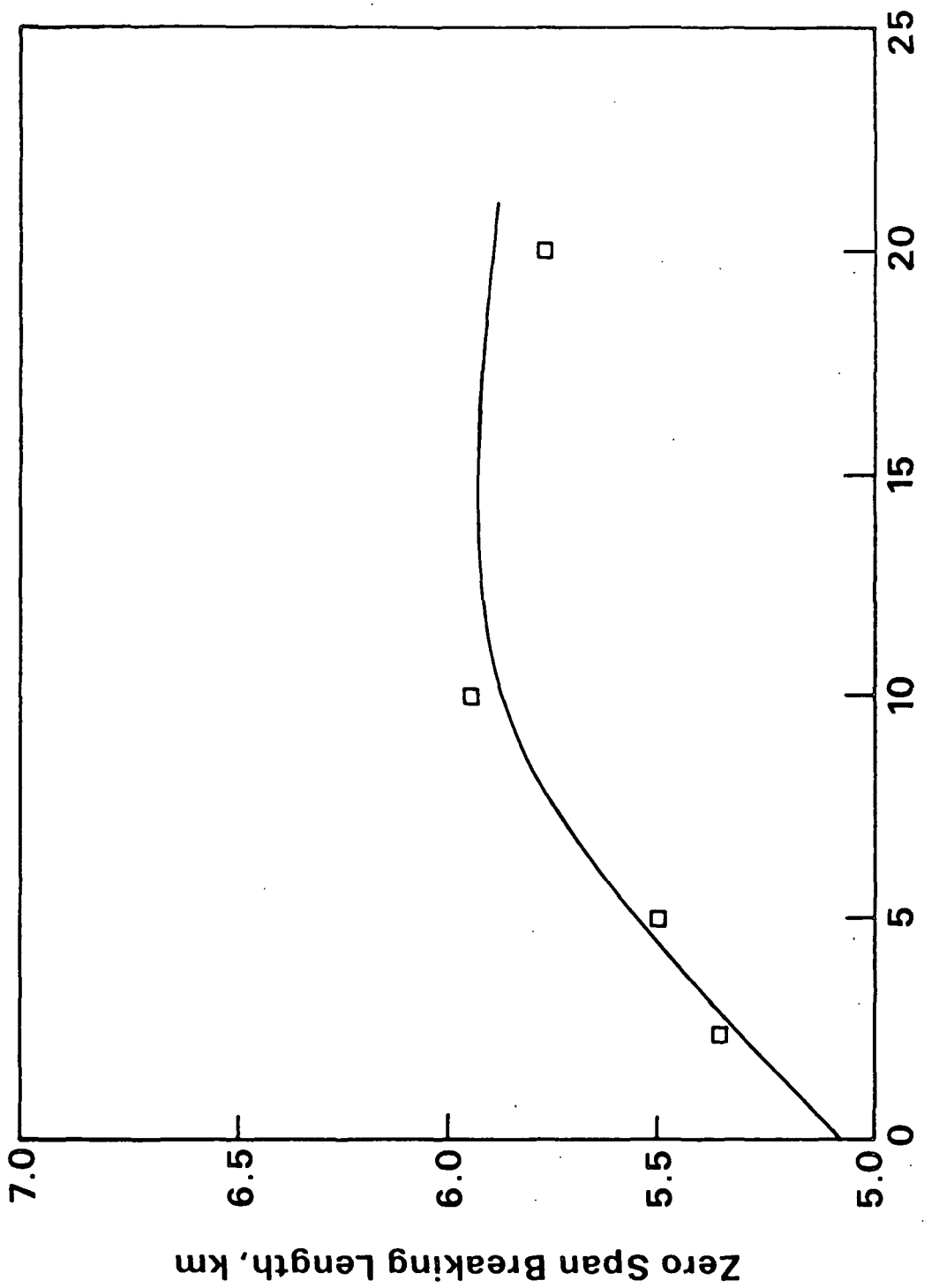


Figure 1. Effect of addition of well-beaten sulfite pulp on zero-span breaking length of coarse southern pine thermomechanical fiber.

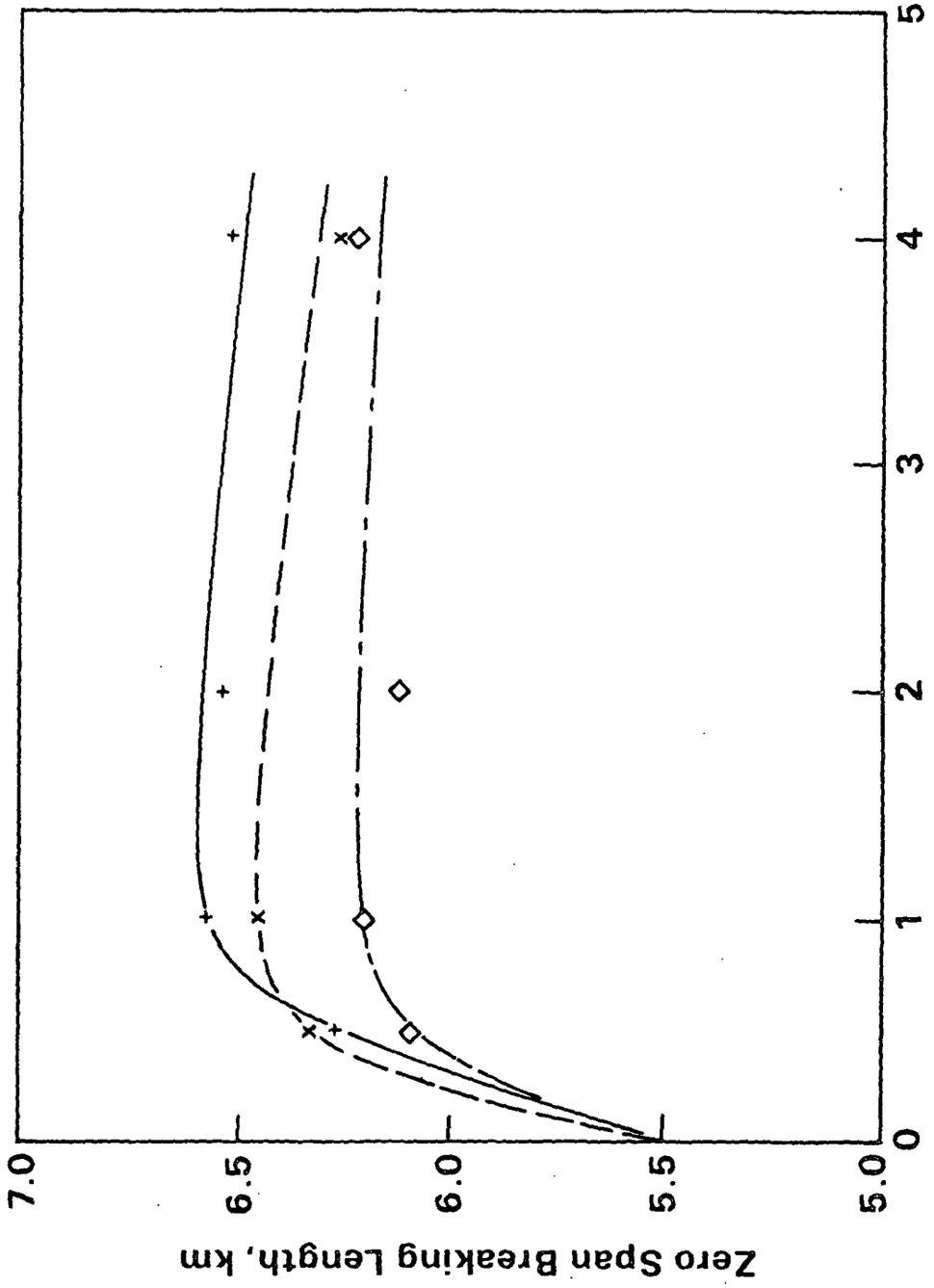


Figure 2. Effect of bonding additives on zero-span breaking length of coarse southern pine thermomechanical fiber. Upper curve: polyamide polyamine epichlorohydrin (PAE); middle curve: cationic starch; lower curve: PAE-CMC.

18.7. This is much lower than the value of 40 km inferred from the single fiber data (which itself is probably too high to be representative of the average strength of all the fibers because of the selection process described above) and moderately lower than the average value of 25 from the thin wood section testing (which may be low, owing to stress concentration effects). It was therefore concluded that either the fibers were being weakened during fiberization, that falsely low zero-span data were being obtained, or both. Likely causes of low zero-span results are insufficient bonding (which results in sensitivity of the result to slippage under the jaws of the tester and minor deviations from true zero-span) and poor formation (which results in uneven clamping and stress concentration).

Figure 3 consists of two light micrographs of specimens which were broken in the zero-span test, showing the rupture line. They suggest that both problems referred to above were present. The failure line is not straight, indicating that some fibers were pulled out and not broken. In addition, formation was very poor, as shown by the existence of many large open areas and bundles of parallel fibers. In the vicinity of the failure line these bundles tended to be oriented parallel to it, suggesting that the more nearly perpendicular ones had been pulled out.

In an attempt to solve the formation problem, samples of accepted fiber were processed for various lengths of time in the British disintegrator. It was hoped that the mechanical action experienced by the fiber bundles in the mixer would be sufficiently vigorous to separate them and sufficiently mild to have little or no effect on the fiber strength. Tables 8 and 9 show the effect of this treatment on the fiber classification and properties of handsheets made from this material. Changes in both categories were slight; there was a decrease in

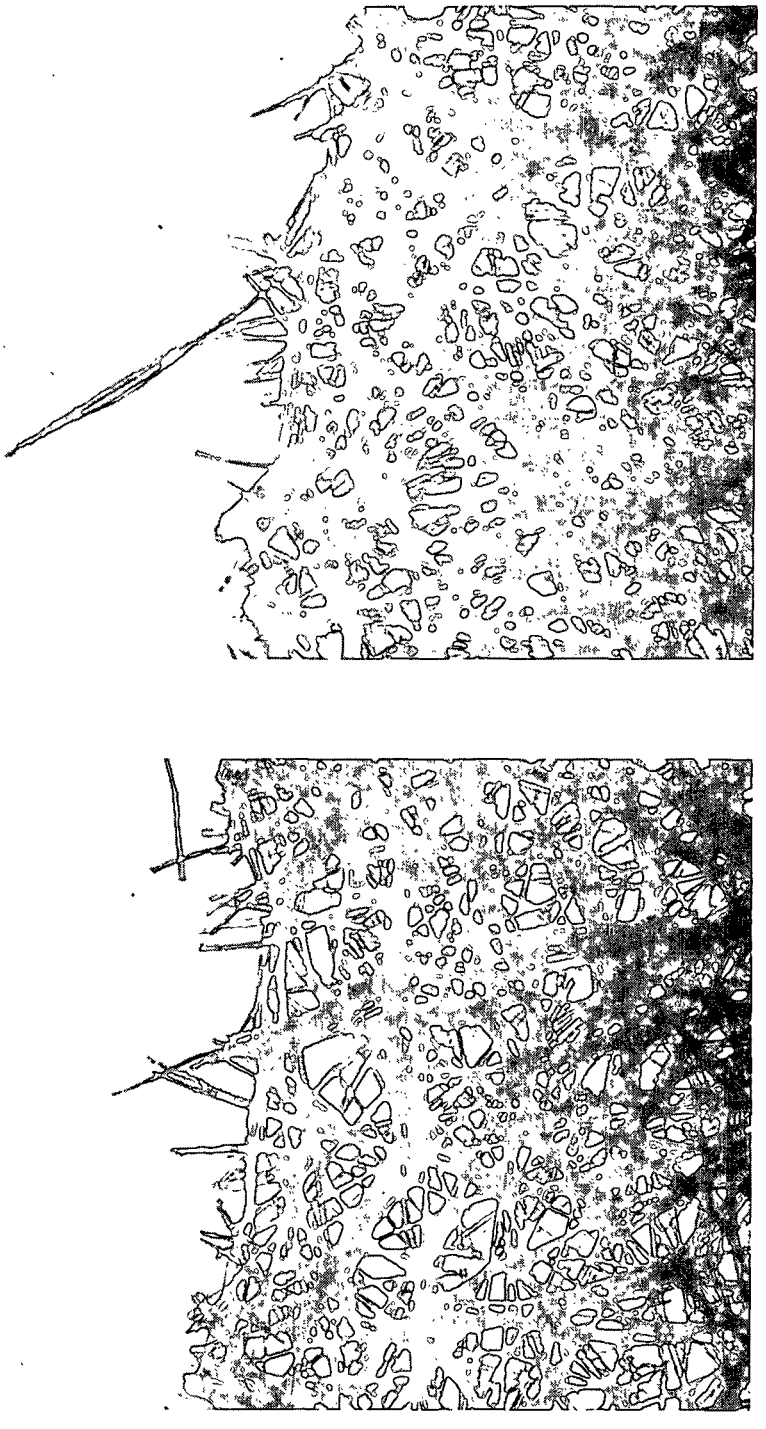


Figure 3. Fiber rupture during zero-span testing.

the 2 coarse fractions and an increase in the middle fraction; there was also a decrease in freeness and increases in formation index and scattering coefficient. A slight improvement in formation is observed after a sixty minute beating as shown by two light micrographs in Fig. 4.

Table 8. Bauer McNett Classification of Asplund pine fibers.

Disintegration Time	On 14 mesh, %	On 28 mesh, %	On 48 mesh, %	On 100 mesh, %	Through 100 mesh, %
0	14	43	25.3	11.7	6
30	13.9	44.7	26.6	11.7	3.1
60	13	40	24.4	10.5	12.1
120	10.7	42.7	27.7	12.1	6.8
180	--	--	--	--	--

Table 9. Handsheet properties of Asplund pine fibers.

Disintegration, Time, min	Freeness, CSF	Zero-span, km	Formation, Thwing	Scattering Coefficient, cm^2/g
0	770	6.8	18.4	169.9
30	770	6.46	21.4	176.0
60	750	6.98	21.9	181.2
120	730	7.03	19.1	164.4
180	625	6.63	23.3	187.6

Shive counts were also done on samples of fiber which had been agitated for various periods in the disintegrator. Figure 5 shows how they responded. The total number of shives decreased by about 40% during the first hour and changed little thereafter. On the other hand, the larger shives (consisting of 6 or more fibers) were not affected, as shown in Fig. 5.

The problem of improving formation and bonding in coarse pine fiber sheets without changing yield or fiber mechanical properties remains. It was set aside so that we could proceed to obtain some information on the behavior of spruce fibers, which are generally easier to deal with than the thicker-walled,

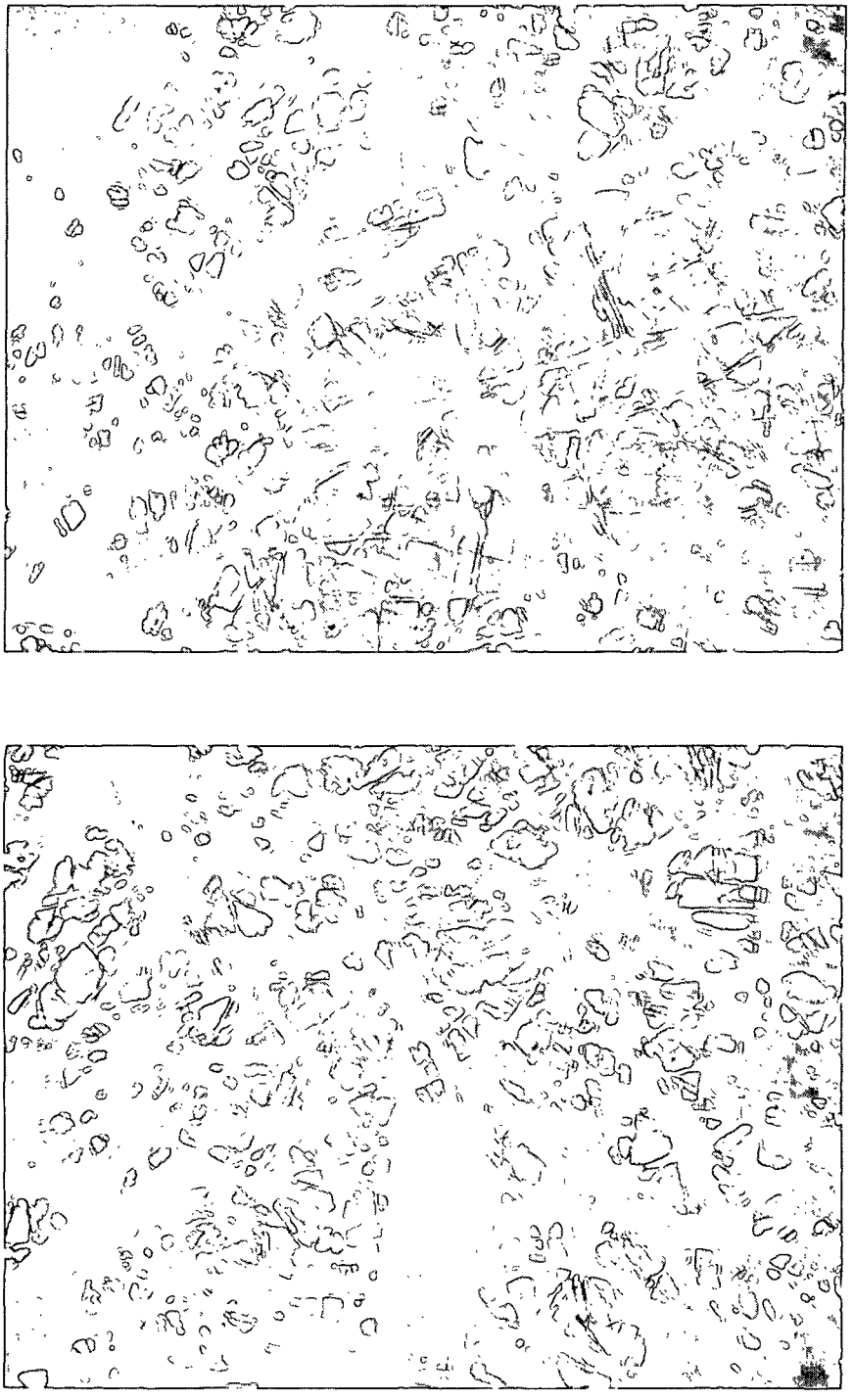


Figure 4. Effect of beating time on the formation of high-yield pine fibers.

more resinous pine fibers. Once again, the objective was to determine the effect of fiber separation under various conditions on fiber properties, with emphasis on fiber strength and, as far as possible to draw inferences concerning the mechanism of fiber separation.

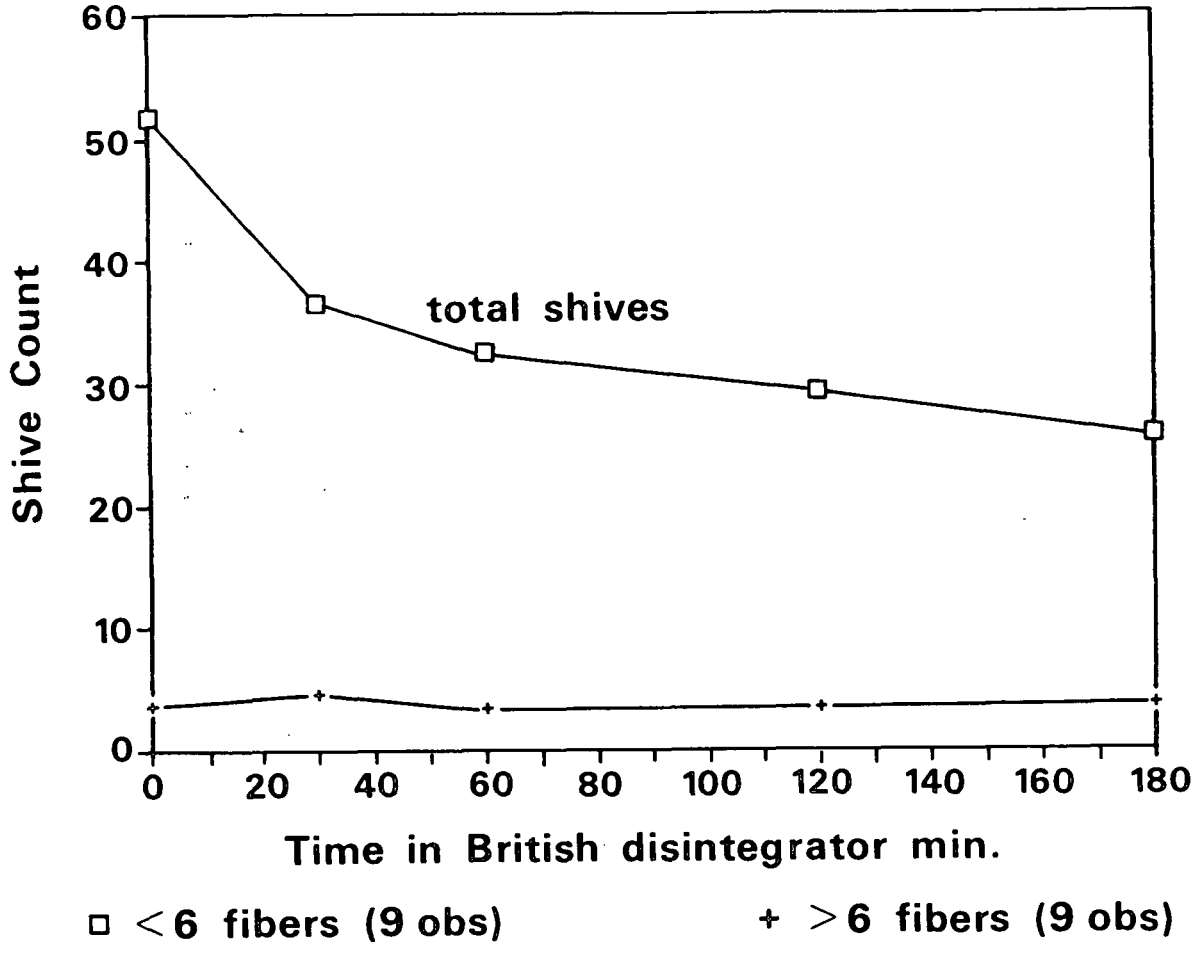


Figure 5. Effect of beating time in the British disintegrator on fiber bundles.

The experimental design adopted for this work was a full factorial comprising three levels of fiberization temperature (80, 120 and 160°C), three levels of fiberization time (1, 2 and 4 minutes), and two levels of sulfonation prior to fiberization (none and 30 min. at 140°C with 120 g/L Na_2SO_3).

To date, the experiments at 120°C with no sulfonation have been completed. Table 10 summarizes classification data for the three pulps. Perhaps the most interesting feature of the data is their constancy with increasing fiberization time. This suggests that the size distribution of the comminuted material is determined at the time of its separation from the wood chips and is not changed thereafter.

Table 10. Bauer McNett classification of spruce wood chips.

Run No.	Fiberization Time, min	Accepts, %	On 14 mesh, %	On 28 mesh, %	On 48 mesh, %	On 100 mesh, %	Through 100 mesh, %
4	1	37.4	23.7	32.9	17.8	7.1	18.5
5	2	48.8	22.4	32.7	18.1	7.1	19.7
6	4	63.4	24.4	32.6	18.3	7.9	19.7

Handsheet properties after various disintegration times are shown in Table 11. Comparisons with the pine data of Table 9 show that the spruce fibers are more readily refined by the action of the disintegrator and exhibit higher zero-span strength. An interesting feature is that the maximum zero-span tensile strength increases with increasing fiberization time, presumably as a result of increased bonding. Nevertheless, this observation suggests that fibers, once separated, do not undergo strength reduction as a result of continued mechanical action.

The highest zero-span value of 9.5, when multiplied by 8/3 to correct for the random fiber orientation, gives 25.3. This value, although higher than the corresponding value of 18.7 for pine, is considerably lower than that to be expected on the basis of the thin wood section measurements (about 39). Further work is needed to determine the extent to which the difference can be attributed

to deficiencies in the zero-span test as an indicator of fiber strength and to find ways of removing those deficiencies.

Table 11. Handsheet properties of spruce refined pulp.

Run No.	Fiberization Time, min	Disintegration Time, min	C.S. Freeness, mL	Zero-span, km	Tensile Index, Nm/g	Burst Index, kPa·m^2/g	Tear Factor	Stiffness, lb/inch	Scattering Coeff., cm^2/g
4	1	0	760	6.81	1.92	0.00	16.9	112	219.39
		60	725	7.86	8.31	0.37	42.9	358	244.78
		120	670	8.47	12.37	0.62	46.9	398	258.08
		180	590	8.30	15.62	0.94	52.9	425	271.90
5	2	0	750	7.31	3.46	0.00	30.2	148	243.49
		60	680	8.52	10.78	0.57	44.4	349	268.08
		120	660	8.36	14.52	0.76	50.0	384	279.32
		180	550	8.75	19.72	1.18	63.7	449	295.64
6	4	0	730	7.56	4.77	0.00	33.3	221	255.43
		60	660	8.56	15.89	0.79	48.0	493	286.30
		120	620	8.31	18.63	1.08	59.3	571	295.34
		180	520	9.46	23.50	1.61	73.5	667	316.99

In the meantime, direct determination of fiber strength, a reliable but tedious method, will be used. The results of such a determination are contained in Table 12. Comparison with the pine data of Table 7 show that the load bearing ability of the spruce fibers is much lower, but so is their cross-sectional area. The result is that the breaking stresses of fibers of the two species are remarkably similar. This is a somewhat unexpected result in view of the decidedly superior strength of the spruce wood sections, and may indicate that spruce fiber strength is reduced in the process of separation and that this occurs to a greater extent than in the case of pine.

Table 12. Single fiber analysis of sample No. 6.

Pulp Type	No. of Fibers	Load, g	C.S.A., μm^2	Stress, kg/mm^2	El. Modulus, kg/mm^2	Strain, %
Spruce	49	11.5 ± 0.8	231 ± 16	54 ± 4	1014 ± 97	7.5 ± 0.4
Pine RMP (Table 7)	43	32 ± 4	582 ± 73	59 ± 8	1111 ± 274	7.2 ± 0.9

CONCLUSIONS

1. Latewood sections of both spruce and pine have about 50% higher longitudinal tensile strength than the corresponding earlywood sections. Spruce sections are 30-50% stronger than pine sections. It may be inferred that the same conclusions hold true for the corresponding fibers.
2. Sulfonation of southern pine earlywood sections does not affect their load bearing ability. This implies that sulfonation does not affect fiber strength. Fiberization of sulfonated southern pine chips gives fibers having the same strength as fibers separated from unsulfonated chips.
3. In the high-yield pine pulps examined, fibers from the 48 mesh fraction were weaker than those from the 28 mesh fraction. This may indicate that reductions in fiber length are accompanied by reductions in fiber strength, or that initially weaker fibers are more likely to be shortened, or both.
4. Sulfonated chemimechanical pulp from southern pine has low strength, showing little or no superiority over the corresponding refiner mechanical pulp.
5. Comparison of high-yield pine pulp single fiber properties with literature data for a pine kraft pulp leads to the tentative conclusion that high-yield fibers have twice the load bearing capacity of kraft fibers.
6. Single fibers from the 28 and 48 mesh fractions of high-yield pine pulps have a higher average breaking length than the wood from which the pulps were made. This is probably the combined result of stress concentrations during the zero-span testing of the wood and the likely superiority of the strengths of the long fibers to those of the remaining pulp elements.
7. Sheets of coarse fibrous material made from southern pine have a zero-span breaking length of about 7 km. This corresponds to a single fiber breaking length of about 19 km, which may be compared to the value of 25 expected on

the basis of wood section test results. The difference is due to a combination of fiber damage associated with fiberization and poor bonding and formation in the zero-span sheets.

8. Single fibers from a coarse spruce mechanical pulp have a breaking length which is about the same as that of the wood from which it was made. This differs from the pine result in a way that suggests that spruce fibers are more susceptible to strength loss during fiberization.

PLANS

1. Complete statistical analysis of existing data and write two membership reports and two publications.
2. Complete the study of effects of fiberization variables on spruce fiber properties.
3. Improve quality of zero-span sheets made from coarse fiber; concentrate on removal of fiber bundles. Attempt to establish an unequivocal relationship between zero-span strength and average single fiber strength.
4. Extend single fiber properties measurement to fiber fragments passing through 48 mesh screen.
5. Determine effect of fiberization conditions on southern pine fiber properties.
6. Determine maximum sheet strength currently achievable by using bonding agents with strong high-yield fibers of the types already produced.
7. Investigate feasibility of relating thin wood section zero-span tensile strength to average single fiber strength by mathematically modelling an assemblage of parallel fibers undergoing tensile failure.
8. Assess usefulness of mathematical models of mechanical behavior of single fibers as a means of setting goals for research on chemical modification of the fiber wall.

9. Conduct initial experiments to evaluate feasibility of improving fiber properties by selective wall component modification.
10. Plan and initiate activity in the areas of (a) correlation of wood properties and fiberization behavior, (b) alternative fiber separation methods, and (c) biological pretreatment of wood. Collaborate with Engineering Division to determine effects of impulse drying on properties of sheets made from coarse high-yield fiber.

ACKNOWLEDGMENTS

The skillful experimental assistance of Kristie Rankin, Cecilia Nordberg, Harry Grady and members of the Paper Testing and Fiber Science Groups is gratefully acknowledged.

REFERENCES

1. Status Report, Project 3566, February, 1984.
2. Status Report, Project 3566, October, 1984.
3. Nordberg, C. M., Independent Studies Report, May 31, 1985.

THE INSTITUTE OF PAPER CHEMISTRY

Thomas J. McDonough
Group Leader, Pulping/Bleaching
Pulping Sciences
Chemical Sciences Division

Salman Aziz
Supervisor, Pulp Laboratory
Pulping Sciences
Chemical Sciences Division

APPENDIX

LITERATURE SEARCH ON APPLICATIONS OF BIOTECHNOLOGY TO HIGH YIELD PULPING PROCESSES

A Report Submitted To:

Dr. Earl Malcolm, Director
Dr. Tom McDonough, Group Leader
Chemical Sciences Division
The Institute of Paper Chemistry
P.O. Box 1039
Appleton, WI 54912

By:

J. V. Maxham, Ph.D., P.E.

Consultant
33 Tracy Court
Appleton, WI 54915
(414)734-2506

May 3, 1985

EXECUTIVE SUMMARY

Biological pulping (retting) and enzymatic pulping of nonwoody plant materials are practical means to produce papermaking fibers. The literature articles reviewed showed that retting times can be as little as 4 days and enzymatic pulping times as little as 4 hours. Enzymatic pulping times, therefore, were not much longer than chemical pulping times. In some instances, the biological/enzymatic pulps produced had a higher yield than a chemical pulp and possessed similar, sometimes superior, mechanical and physical properties.

Experimental results reported in the literature where microorganisms (principally white-rot fungi) were grown on wood chips or on coarse mechanical pulp were not encouraging. Pulping times were at least two weeks and therefore excessive. Microbial attack was sometimes beneficial in substantially increasing the water retention value of the pulp or reducing the refining energy input to achieve a given freeness level or strength index. Microbial pulping also resulted in little wood weight loss, typically less than 2%.

Several different microbial species (both bacteria and fungi) have been isolated that possess wood delignifying capabilities. The technology now exists to splice the DNA segments responsible for delignifying enzyme replication from these organisms into the fast growing E. coli. A genetically engineered E. coli could, in theory, produce the enzyme in substantial quantities at a reasonable price. One researcher has in fact successfully cloned a delignifying enzyme gene into an E. coli.

This biotechnological breakthrough suggests that concentrated delignifying enzyme solutions may soon be available for experimental purposes. Pulp and Paper Industry interest in enzymatic pulping will encourage the high tech biotechnology firms to produce experimental pulping enzyme solutions. IPC would be

an ideal place to evaluate such enzyme products. IPC, therefore, should consider initiation of a modest biopulping research project in conjunction with the High Yield Pulping project. The goal of the biopulping project would be to produce a high yield and high strength pulp with minimal energy input by digesting wood chips or coarse mechanical pulp with delignifying enzyme solutions.

The areas of enzymatic wood pulping and enzymatic modification of wood pulp appear to be very promising. If the experience with enzymatic pulping of nonwood plant materials can be extrapolated to wood, it is expected that the enzymatic pulping rate will be comparable to chemical pulping rates. Enzymatic pulping yields are expected to be higher than chemical pulping yields with no deterioration of mechanical and strength properties. This is because enzymatic reactions are usually very specific: only certain bonds in the lignin molecule would be cleaved with little or no attack on the cellulose and hemicellulose. This would be done with very little enzymatic pulping energy input since the pulping would probably be carried out at a temperature below 40°C.

Because enzymatic pulping promises to result in substantial energy savings, a logical source of outside funding for a biopulping project would be the Department of Energy.

INTRODUCTION

The principal objective of the High Yield Pulping project at IPC is to research methods that produce pulps with high yield, strength, conformability, and brightness, while minimizing the pulping energy input. The current emphasis of the High Yield Pulping project are pulping techniques that result in a high yield and high strength pulp. Producing a pulp with both high yield and strength is a difficult proposition. Conventional pulping processes that produce pulp

with high yield (e.g., groundwood pulping) invariably result in a low strength pulp. The converse of this is true since a low yield pulping process (e.g., Kraft and sulfite chemical pulping) normally results in a high strength pulp. Chemimechanical processes produce pulps of intermediate yield and strength. It appears that the more lignin contained in the pulp, the lower the pulp strength.

A pulping process that produces a pulp with both high yield and strength requires that the middle lamella lignin be degraded only slightly; enough to allow easy separation of the fibers in a mechanical defiberizing process. Once separated, the lignin containing fibers must be modified to allow the fibers to collapse to create high fiber contact area.

It is of interest to conduct a literature search of biotechnological wood pulping techniques. Microorganisms produce enzymes that catalyze specific biochemical reactions. By isolating microbial delignifying enzymes that break specific lignin bonds, it might be possible to first digest wood chips with a delignifying enzyme solution then separate the fibers essentially intact in a mechanical process with little lignin removal and low energy input. Other enzymes could be used to treat the defiberized pulp to modify fiber surface properties. The possibilities of biological/enzymatic pulping are intriguing and should be investigated.

This report begins by first reviewing current applications of biotechnology to the Pulp and Paper Industry. These applications include the retting and enzymatic pulping of non-woody plant materials, starch enzymatic conversion in papermaking, and biological wastewater treatment. Research into the biological pulping of wood is then reviewed. Though the biological/enzymatic pulping of wood is in the R&D stage with little promise to become commercially viable in the near future, recent biotechnological breakthroughs

ensure the eventual introduction of biotechnological pulping and bleaching processes to the Pulp and Paper Industry.

CURRENT APPLICATIONS OF BIOTECHNOLOGY TO THE PULP AND PAPER INDUSTRY

Retting and Enzymatic Pulping of Nonwoody Plant Tissue

Retting has been used for several thousand years to free cellulose fibers from nonwoody plant tissue. Stanier et al.[1] gives a brief description of this ancient process first used to free the bast fibers from flax and hemp. Plant stems are first immersed in vats of water. As they become waterlogged, anaerobic butyric acid bacteria develop which rapidly attack the plant pectin material that cements the bast fibers together. Once the stem structure is sufficiently loosened, the retting process is halted. Unduly prolonging the retting process results in the formation of the cellulose fermenting bacteria which will destroy the bast fibers.

Retting and enzymatic processes are used today in Japan to pulp nonwoody plant tissue. Several recent articles by Kobayashi and Matsuo[2-7] of the Government Industrial Research Institute, Shikoku, Japan were reviewed that relate to this subject. One of the articles[2] looked at the enzymatic pulping of decorticated pineapple leaf fiber. Four commercially available enzyme solutions were evaluated. Two of the enzyme solutions mainly attacked pectin (pectinases); the other two enzyme solutions mainly attacked cellulose (cellulases). The enzymatic pulping temperature was 37°C, enzyme concentration was 0.1%, leaf consistency was 3.0%, and the pH was in the range of 2.0-5.0. Pulping times of 3, 5, and 24 hours were investigated. A chemical pulp was also prepared to serve as a comparison. The chemical pulp was made by cooking the pineapple leaf fiber in a autoclave containing NaOH solution at 150°C for 1 hour at a liquor to fiber

ratio of 7 and alkali ratio of 0.15. The pulping yields of the pectinase pulps were in the range of 72.8-87.8% and compared favorably with the chemical pulp yield of 74.3%. The cellulase pulp yields were much lower (46.0-78.0%). In general, the physical properties of handsheets of the enzymatic pulps were inferior to that of the chemical pulp. At a given freeness level, the bulk density of the pectinase pulps were about the same as the chemical pulp though the breaking length was about one-half that of the chemical pulp. The cellulase pulps had lower bulk densities and breaking lengths than either the chemical or pectinase pulps. The enzymatic pulps had lower tear and burst factors than the chemical pulp.

In another article,[3] Kobayashi and Matsuo looked at the enzymatic pulping of mitsumata bast fiber by two commercially available pectinase solutions. Mitsumata contained considerably more pectic substance (8.6-14.8%) than pineapple leaf fiber (1.2%) and therefore it was expected that the two pectinase solutions would be more successful in pulping mitsumata than pineapple leaf fiber. Pulping conditions were similar to that mentioned above. The pectinase pulp yields were in the range of 66-82% and compared favorably with the chemical pulp yield of 53%. The highest yields were obtained when the enzyme concentration was low (0.025%) and pulping time was low (4 hours). Both the average fiber length and single fiber strength of one of the pectinase pulps was slightly higher than the chemical pulp. The zero-span tensile strength, however, of the pectinase pulps were somewhat lower than the chemical pulp. The physical properties of handsheets were measured. The bulk density of the enzymatic pulps was about the same as the chemical pulp but the breaking length was 18-30% less. The tear factor of the enzymatic pulps were superior to the chemical pulp. The burst factor of the enzymatic pulps were inferior to the chemical pulp when

enzyme concentration was low (0.025-.10%) but about the same at high enzyme concentrations (1.0%). The folding endurance of the chemical pulp was superior to the enzymatic pulp which was attributed to the higher lignin content of the enzymatic pulps. A key point of this article is the fact that the mitsumata was sufficiently pulped enzymatically in 24 hours at a low enzyme concentration (0.025%). Increasing the enzyme concentration up to 1.0% reduced the pulping time to as low as 4 hours.

Two articles[4,5] by Kobayashi and Matsuo gave results in the enzymatic pulping of mitsumata under alkaline conditions. Alkaline conditions cause swelling of the bast thereby increasing the enzyme penetration rate. Alkaline tolerant pectolytic enzyme solutions were obtained by growing bacterial cultures of Erwinia and Streptomyces. Enzymatic pulps with nearly the same quality of chemical pulp were made in only 5-7 hours with the enzyme solutions of two species of Erwinia. The pulping temperature for the Erwinia species was only 30°C. The yields were not given. Though mitsumata was successfully pulped with Erwinia enzyme solutions, Cuban and Thai kenaf were not effectively pulped. This was attributed to the much higher lignin content of kenaf compared to mitsumata.

Kobayashi et al.[6] gave results in the alkaline enzymatic pulping of kozo (paper mulberry) using an enzyme solution of Erwinia. Pulping was carried out at 30°C for up to 24 hours. The enzymatic pulp papers proved to be superior to the chemical pulp papers in many respects. The enzymatic pulp paper had greater homogeniety in basis weight, better dynamic printing smoothness and superior brightness. The zero-span tensile strength, breaking length, tear factor, and folding endurance of enzymatic pulp fibers were about the same as the chemical pulp.

Yoshihara and Kobayashi[7] examined the retting of mitsumata under alkaline conditions using a Bacillus. The optimum concentration of sodium carbonate was 1.0-1.5% yielding an initial pH of 10.1-10.3. The retting temperature was 30°C. Under optimum conditions, the retting was completed in about 4 days with an overall pulp yield of approximately 70%. This yield was about 10% higher than the chemical pulp yield. The physical strength properties of the paper sheets made from the retted pulp were comparable, and in some cases superior to those of the paper made from chemical pulp. The retted sheets exhibited good formation and the surface of the sheets was milder and softer than the chemical pulp sheets.

Retting and enzymatic pulping are similar in the respect that enzymes secreted by microorganisms are used to attack the plant material (e.g., pectin) that cements the cellulose fibers together. In retting, the microorganisms are allowed to grow directly on the plant material. Retting times are quite long due to the fact that substantial time is necessary to grow the biomass from the initial inoculum. Increasing the inoculum amount should substantially decrease retting time. Probably 1-2 days would be sufficient. In enzymatic pulping, only enzyme solutions are allowed to contact the plant materials. The results contained in the literature articles reviewed, show that pulping times are generally less than a day and as low as a few hours. This makes enzymatic pulping times for nonwoody plant materials about the same as for chemical pulping.

Enzymatic pulping has a distinct energy advantage compared to chemical pulping since the pulping is carried out at moderate temperatures. Enzymatic pulp yields tend to be higher than chemical pulp yields and the physical properties of enzymatic pulp handsheets are sometimes superior to those of chemical pulp. It is critical, however, to select the proper enzyme(s) to pulp the raw

material. A particular enzyme or enzyme solution that works well for one particular raw material will not work well on another.

It is worthy to notice that enzyme solutions were prepared in some cases by growing wild type bacterial strains in pure culture then separating the cell suspension from the culture fluid. The culture fluid was then used as the enzymatic pulping solution. The first task in this process is to isolate promising bacterial cultures from the environment. Yoshihara and Kobayashi[7] isolated about 800 bacterial strains from soil, sewage, and decomposed manure before selecting the few strains used in their retting experiments. In this case, the strains had to be alkaline tolerant since alkaline conditions were favorable to speeding up the retting process. The next task in enzymatic pulping is to grow the bacterial stain in pure culture under conditions that optimize the production of enzyme. The process can either be batch or continuous. Separating the cells from the culture fluid may not be necessary. The enzyme solution could be concentrated if neccessary by employing membrane separation technology.

The tasks associated with producing enzyme solutions are well established and are known to the microbiologist and biochemical engineer. The key question is whether the economics of enzymatic pulping compare favorably with chemical pulping. The answer is probably yes if the enzymatic pulping yield is higher than the chemical pulping yield and the properties of the two pulps are similar. However, the cost of producing the enzyme will be high. This cost is ameliorated by the fact that little enzyme is required for pulping and that the enzyme can be reused. The low energy requirement of enzymatic pulping will also help keep total pulping costs down.

Enzyme Conversion of Starch in the Paper Mill

Starch has been used for many years in papermaking as a surface sizing or a coating binder. However, in order to use starch for this purpose its viscosity must be reduced. Either a thermochemical or enzymatic process can be used to reduce starch viscosity. Mayatt[8] reviewed the enzymatic processes used to convert starch as currently practiced. Enzymatic conversion of starch was first introduced into the Paper Industry in the early 1960's. It is estimated that 30% of all starch used is now enzyme converted.

Amylases are the enzymes responsible for starch conversion and are produced by both bacteria and fungi. Amylase solutions are available commercially and can be obtained to fit a specific application. A paper mill, in general, does not culture its own bacteria or fungi to produce amylase but purchases it from a supplier. Mayatt claims that the payback period in converting from a thermochemical to enzymatic starch conversion system can be as short as a few months.

Typically very little enzyme solution is required to convert starch. Mayatt gives a typical enzyme conversion program where 50 mL of a fungal enzyme solution is added to 1000 kg of potato starch and 4000 liters of water. This shows that an enzyme solution can have a very high activity.

The enzymatic conversion of starch is an example showing that enzymatic processes are competitive with thermochemical processes once enzymes with the right properties are available. It can be speculated that once enzymatic pulping processes become developed, the Pulp Mill would probably purchase the enzyme solutions from an outside supplier rather than make its own enzyme solutions from scratch by culturing microorganisms.

Biological Wastewater Treatment

The most prevalent application of biotechnology in the Pulp and Paper industry is the treatment of wastewaters for environmental protection. Biological treatment processes such as lagoons and activated sludge processes are used to remove soluble organic materials from wastewaters after settleable solids are first removed by sedimentation. It is significant that physical-chemical processes are not economical in comparison to biological processes in wastewater treatment. This is in spite of the fact that the physical size of a biological process is often much larger than a physical-chemical process that can accomplish the same task. The advantage of the biological process lies in its simplicity of design and operation, low maintenance requirements, and tolerance (within limits) of variations of wastewater flow and composition. It can be speculated that a biological pulping process may enjoy many of these same advantages but would have a rather large physical volume.

Other Potential Applications

A potential biotechnology application is the pulping of wood, the major raw material by far to produce paper products. The remainder of this report will be devoted to this subject. Other potential applications include the biological/enzymatic bleaching of pulp and treatment of effluents containing lignin-derived wastes. The lignin wastes would either be destroyed by a biological/enzymatic process or converted to useful chemicals.

BIOLOGICAL AND ENZYMATIC PULPING OF WOOD

Introduction

It is conceivable that a biological or enzymatic pulping process could be developed for wood that would be similiar in principle to the retting and enzymatic pulping processes described previously for nonwoody plant materials.

Zaborsky[9] summarized the incentives to develop a biological/enzymatic delignification process and the drawbacks associated with present chemical/physical delignificaton processes. These are presented in Table 1.

Table 1.

Drawbacks of Present Delignification Processes (Chemical, Physical)

- Energy intensive
- Environmental incompatibility
- Moderate resource utilization (conversion yield)
- High consumption of chemicals
- Sulfur-containing lignin products

Incentives of a Biological/Enzymatic Delignification Process

- High selectivity and activity of enzymes
- Low conventional energy requirement
- Environmental compatibility
- Renewable catalysts
- Nonsulfur-containing lignin products

Presumedly, a definate advantage that a chemical delignification process would have over a biological/enzymatic process would be a high reaction rate. The high temperature and harsh chemical environment of a Kraft or sulfite process serves to delignify wood at a relatively rapid rate. A biological/enzymatic pulping process would probably be conducted at a temperature in the range of 25-40°C though thermophilic microorganisms exist that can grow at temperatures up to around 70°C. The enzymes produced by these organisms are also tolerant of high temperatures. It is likely, however, that the biological/enzymatic pulping would proceed at a much lower rate than a chemical

pulping process due mainly to the lower temperature. This means that a biological/enzymatic pulping reactor would be very large in comparison to a chemical pulping reactor. Nevertheless, the biological/enzymatic reactor may be less expensive than the chemical pulping reactor because the low temperature and pressure pulping would result in a simple reactor design and relatively inexpensive materials of construction.

The fact that enzymatic pulping of nonwoody plant materials proceeds at a rate similar to chemical pulping may be evidence that a enzymatic pulping process for wood will not be much slower than a chemical pulping process. The key to the successful enzymatic pulping of wood is the production of delignifying enzyme solutions that have a high activity toward the wood pulped. These enzyme solutions need not be produced at the mill but could be purchased from a supplier.

In the biological/enzymatic pulping of wood, it would be essential to first debark and chip the roundwood as done conventionally. At this point several different biological/enzymatic pulping schemes can be imagined. For example the biological/enzymatic pulping could proceed in an existing chip pile by sprinkling the top of the chip pile with a biological/enzyme solution. The solution would trickle through the pile and be collected at the bottom. A portion of the solution would be wasted with the remainder recycled and supplemented with fresh solution. Unfortunately, it would be difficult in this approach to ensure uniform contact of the chips with the solution and to prevent undesirable microbial growth from occuring. It would be better to have a chip tower dedicated to the purpose of contacting the microbial/enzyme solution with the chips. Steaming the chips prior to introducing them to the tower would sterilize the chips preventing undesirable microbial growth from occurring and allowing better penetration of the biological/enzyme solution.

It is also possible to carry out the biological/enzymatic pulping in vessels that allow the chips to be completely submerged in the biological/enzyme solution. Hopefully, the reaction would proceed quickly enough to allow the use of existing chemical pulping vessels. In biological pulping, the vessel would need to be aerated since the delignification reaction is oxidative.

Whether a chip tower or submerged vessel is used, the options available in biological/enzymatic pulping are: 1. Grow the microorganisms directly on the chips from an initial innoculum. 2. Grow the microorganisms in a separate process and contact the chips with the culture fluid that contains the appropriate enzymes. 3. Purchase concentrated enzyme solutions and make-up the pulping solution. Later on when the literature on biological wood pulping is reviewed, it will be seen that the main approach has been to grow the organisms directly on the wood chips. This is probably the least desirable of the three approaches. One reason is that the wood pulp will be contaminated with biomass that probably will not enhance the pulp quality. The pulping process rate will probably be slower as evidenced by the difference in rates between retting and enzymatic pulping of nonwoody plant materials. However, the enzymatic delignification of wood is a complex process requiring several different enzymes. Developing the appropriate enzyme solutions will be a difficult task. Comparing approaches 2 and 3, a mill would probably opt for purchasing the enzyme solution if the price is right. However, waste streams exist in an integated mill (e.g., excess whitewater) that contains nutrients needed to grow a microbial culture. These waste streams could conceiveably be utilized as a "free" raw material to grow the microbial suspensions. Pure culture conditions though need to be maintained making utilization of the waste materials difficult. Probably the glucose and other nutrients needed to grow the microorganisms would be purchased or made from wood fiber by hydrolysis.

Biological/enzymatic pulping would require a mill to hire a substantial staff competent in microbiology and biochemical engineering unless the enzyme solutions could be purchased from a supplier. It is therefore likely that the biological/enzymatic pulping development work will be left to the high tech biotechnology firms who would later profit by selling the appropriate enzyme solutions. In this regard there has been many significant advances in the biotechnology area. Now enzymes and other complex biomolecules can be produced cheaply and in quantity by using gene splicing techniques. In this technique, the DNA segment in a gene that replicates the biomolecule, is spliced out and inserted in the DNA of a fast growing bacteria (e.g., Escherichia coli, a human intestial organism). The DNA segment can come from any organism, even a human being. Genentech successfully markets a genetically engineered product.[40] It is human insulin derived by splicing a human insulin gene into E. coli and then culturing the microorganism. There was a report in Chemical and Engineering News[10] about a microbiologist at Louisiana State University, V. R. Srinivasan, that spliced a lignin degrading enzyme into E. coli. The enzyme cleaves both alkyl and aryl-aryl ether linkages in lignin. The enzyme can supposedly degrade lignin in two hours. This appears to be a significant breakthrough that may lead to the commercialization of biochemical pulping.

The biological/enzymatic pulping could be conducted to achieve nearly complete delignification or only partial delignification. For high yield pulping only partial delignification would be required. Steaming and presoaking the chips in alkaline solution may be beneficial in speeding up the biological/enzymatic degradation. The hoped for advantage of an enzymatic degradation compared to a chemical degradation would be that only specific lignin bonds would be broken allowing the fibers to be easily separated without substantial loss of

the hemicellulose and cellulose and with little defiberization energy input. An enzymatic pulping process would be very similar to conventional chemimechanical pulping processes.

After defiberizing and washing the pulp, enzyme solutions could be used to alter the fiber surface properties before refining. Bleaching with enzymes is also a possibility.

Currently biological/enzymatic wood pulping technology is in a nascent stage. Many investigators, however, have performed research in this area and the results of their studies will now be reviewed.

Biological Wood Pulping Literature

Karl-Erik Eriksson of the Swedish Forest Products Research Laboratory in Stockholm, Sweden is one of the world's leading researchers in the area of biological delignification of wood. Eriksson and co-workers have published a number of articles[11-15] relating to the subject of biological pulping of wood. In a paper presented at the 1976 Weyerhaeuser Biological Delignification Symposium,[11] Eriksson reported results obtained in treatment of pine chips for one month with a cellulase-less mutant of Sporotrichum pulverulentum, a white-rot fungus. About two percent of the lignin was removed in this time period. The breaking length, burst index, and tear index of a mechanical pulp made from fungal treated pine chips was 20 to 30% higher than a mechanical pulp made from untreated pine chips. In this paper, Eriksson describes his patented biological delignification process which has yet to be commercially exploited. The chips enter a very large tower that allows an average residence time of 7 days. The chips in the tower are continuously sprayed with a mutant microbial solution. The microbial solution is produced in a separate fermentor where presumedly pure

culture conditions are maintained. The fermentor is fed a solution of sugars from a substrate tank. The sugar solution could be excess whitewater from the paper mill. For a 500 ton/day mill, Eriksson estimates that the tower volume would be 15,000 m^3, the fermentor volume would be 25 m^3, and the substrate tank volume would be 150 m^3. After treatment with the mutant fungus for one week, the chips would be mechanically refined. Eriksson claimed that biological pretreatment of the chips results in substantial energy savings in mechanical pulping that justifies the capital investment.

In another article,[12] Eriksson describes results obtained in a 20 liter composting apparatus where birch and pine chips were rotted with the cellulase-less mutant of S. pulverulentum for a two week period. The chips were then steamed and mechanically refined. A maximum weight loss of 2.5% occurred with pine chips. At that weight loss, the refining energy was 30% less than the control when refining was carried down to a freeness level of 435 CSF. However, when refining was carried down to a freeness level of 125 CSF, the energy saving was only 10%. The energy savings where less significant for pine chips rotted at weight losses of 0.7 and 1.5%. In studies of fungal rotting of birch chips, about a 30% energy saving was estimated when refining to a freeness level of 650 CSF. The mechanical pulp produced from birch wood had very low strength. No difference in strength value was observed between rotted and nonrotted chips. The paper sheets form the rotted chips had a 3 to 4% lower brightness value. For pine chips, the strength properties, tear and tensile indices were the same for pulp from rotted and nonrotted pine chips. The brightness of the pulp from the rotted chips was, however, 7 to 8% lower.

Eriksson et al.[13] described results obtained in rotting pine wood chips and fiberized pulp with wild-type and cellulase-less mutants of Phlebia radiata,

a white-rot fungus. Treating pine wood chips with wild-type fungus for a two week period, resulted in the same tensile index at a given refiner energy input as untreated wood chips. Fungal treatment of fiberized pulp resulted in lower tensile index at a given refiner energy input. Therefore, fungal treatment was not beneficial in improving pulp strength properties at a given refiner energy input. When pine chips and fiberized pulp was treated with a cellulase-less mutant, the tensile index at a given refiner energy input for both treated pine chips and fiberized pulp was the same as untreated pulp. Carrying out the defiberization at 170°C instead of at 127°C, caused the tensile index to increase for both mutant fungi treated pine chips and fiberized pulp in comparison to the untreated pulp. Fungal treatment also affected pulp beatability. Less energy was required to beat the fungal treated pulp to a given freeness level. However, fungal treated pulp had a lower strength than an untreated pulp at a given freeness level. Also, the fungal treated pulps had a lower brightness than the untreated pulp. By and large, these results did not give much justification for fungal treatment of chips or fiberized pulp.

Somewhat more encouraging results were obtained by Eriksson[14] in a later study with the cellulase-less mutant of S. pulverulentum. Eriksson first impregnated the pine wood chips with glucose to a 1.7 wt% level. This prevented substantial hemicellulose degradation during delignification. The chips were rotted for 2 weeks before defibration and refining. Wood weight loss was less than 1% after rotting. In order to obtain a given tensile index on refining, the rotted chips required about 23% less energy than the untreated chips. Fungal treatment of nonimprenated wood, however, did not result in any energy savings. In all cases, the fungus treated pulp suffered loss of brightness compared to the reference pulp.

T. Kent Kirk of the USDA Forest Products Laboratory has a very active research group in the biological delignification area and has published extensively. Five articles[16-20] by Kirk were found where the subject of biological pulping was mentioned. Though these articles mainly reviewed the work done by other researchers, one article[18] presented the results of experiments performed in Kirk's laboratory. Coarse thermomechanical pulp was treated with a white-rot fungus (Phanerochaete chrysosporium) for a 2 week period. Glucose was added to pulp to suppress degradation of the cellulose and hemicellulose. Energy requirements for refining the fungus-treated pulp to develop a given freeness were decreased by 25-30% compared to those of the control. Energy requirements for refining the fungus-treated pulp to develop a given freeness were decreased by 50% compared to those of the control after swelling in alkali. These results were obtained without any loss in pulp strength properties. The fungus treatment reduced the lignin content of the TMP by 19% with no loss in total carbohydrates. If glucose was not added, no energy advantages were gained. Pulp brightness was not affected by the fungal treatment. These results were much more encouraging than the results obtained by Eriksson and coworkers.

In another article,[20] Kirk mentions the fact that several researchers have isolated crude delignifying enzyme solutions from microbial cultures. This may pave the way to development of enzymatic pulping techniques for wood.

Fukuzumi[21] made pulps from rotted chips of the fungus Quercus serrata. In the abstract of this article, it is claimed that the strength and brightness of the fungal pulp was somewhat superior to a control chemical pulp.

Pilon et al.[22,23] grew several species of fungi on refiner mechanical pulp. It was observed that the water retention value (an indirect measurement of pulp mechanical properties) of the pulp increased by the fungal treatments.

The best result was obtained with the white-rot fungus, Schizophyllum commune. The water retention value increased by 88% after 14 days incubation with this organism.

These results show that direct fungal growth on wood chips and wood pulp can result in refining energy savings without deterioration in pulp quality in some cases. However, treatment times appear to be excessive. It is not known to what extent the treatment time can be reduced. Erikkson[11] believes that a treatment time of one-week is possible. If this is the best that can be done, the future of biological pulping would not appear to be very bright. However, the results of biological pulping are encouraging enough to suggest that an enzymatic treatment of wood chips or wood pulp might be very successful if the right enzymes could be isolated, produced in substantial quantities, and concentrated.

Basic Research in Lignin Biodegradation

Studying the basic mechanisms of microbial degradation of lignin occupies the time of many talented researchers throughout the world. The most notable among them are Eriksson of the Swedish Forest Products Laboratory, Kirk of the USDA Forest Products Laboratory, R. Crawford of the Gray Freshwater Biological Institute, D. Crawford of the University of Idaho, Chang of North Carolina State University, Higuchi of Kyoto University, and Fukuzumi of the University of Tokyo. It is easy to justify the importance of research in this area. Lignin is one of the most abundant biopolymers produced in the world. It is also one of the most difficult to biologically degrade. It is of interest to determine how the complex lignin molecule is broken down to carbon dioxide and water and thereby recycled in nature. Lignin is also believed to be the principal precursor of coal and oil. It is of interest to study how lignin is converted

(probably with the help of microorganisms) to these fossil fuels. Possible applications of knowledge accumulated about microbial lignin biodegradation include biological/enzymatic pulping and bleaching, conversion of lignin into industrially important chemicals, improving the food value of lignocellulosic materials used as animal feed, and new wastewater treatment processes to handle lignin containing wastewater.

The proceedings of a symposium on biological delignification sponsored by Weyerhaeuser in 1976[24] has papers given by Eriksson, Kirk, R. Crawford, and Pulp and Paper Industry researchers (e.g., Abson, Guthrie, Eudy, Procter, and Wollwage). Industrial research in biological delignification was minimal with the focus on removing color from Kraft pulp mill effluents using lignin degrading microorganisms. An international seminar on lignin biodegradation was held at the USDA Forest Products Laboratory in Madison, Wisconsin on May 9 to 11, 1978. The proceedings of that seminar were published in 1980.[25] The Weyerhaeuser and USDA proceedings provided an excellent introduction to the technical literature on lignin biodegradation which is quite extensive. The author also reviewed other articles[27-39] in the technical literature on lignin biodegradation that were recently published and were thought to contain significant information. Several of these articles[32-39] were presented at the 1983 International Symposium of Wood and Pulping Chemistry in Japan. An article by Crawford and Crawford[26] provided a good review of current knowledge concerning the microbial degradation of lignin. Most of the information that follows was based on the information presented in that article.

Lignin biodegradation is predominantly an aerobic process (i.e., requires oxygen). A microbial culture that can degrade lignin anaerobically has yet to be isolated though many low molecular weight aromatic compounds are

readily degraded by anaerobic microorganisms. Perhaps in nature, anaerobic microorganisms assist in lignin biodegradation by metabolizing low molecular weight lignin fragments that have been produced by aerobic microorganisms in depolymerizing the lignin macromolecules.

The range of aerobic microorganisms now known to degrade lignin includes a wide variety of both fungi and bacteria. However, only a few kinds of microorganisms (e.g., the white-rot fungi) have the enzymatic capability to attack all the varied structural components of the complex lignin molecule and therefore degrade lignin completely. Other microorganisms only partially attack lignin producing fragments that cannot be further metabolized. The microorganisms that only partially attack lignin would need to form symbiotic relationships with other microorganisms to achieve complete lignin degradation. Formation of humic materials is probably the result of partial attack of lignin by microorganisms.

Of the lignin degrading microorganisms, the fungi have been the most extensively studied. The three main groups capable of degrading lignin are the soft-rot, the brown-rot, and the white-rot fungi. As a rule, both the soft-rot and brown-rot fungi will preferentially attack the cellulose or hemicellulose in wood before the lignin and then will only incompletely attack lignin. The white-rot fungi are the only microorganisms proven capable of totally degrading all the major components of wood to carbon dioxide and water. In white-rot attack on lignin, initially the number of aliphatic and phenol hydroxyl groups are reduced while carboxyl and carbonyl groups increase. Extensive demethylation also occurs and aromatic rings are opened. Both oxygenases and dioxygenases are implicated in these lignin degrading reactions.

It appears necessary for carbohydrate (e.g., cellulose, glucose, etc.) to be present in order for a white-rot organism to degrade lignin. The carbohydrate serves as a growth substrate. Lignin by itself will not support microbial growth. This is certainly a serious drawback as concerns development of a biological wood pulping process. In order to degrade lignin, the organism must be allowed to degrade a portion of the cellulose or hemicelulose in the wood or carbohydrate must be added to satisfy growth needs. It has also been shown that the nitrogen concentration in the growth media is important in lignin degradation. Depletion of the nitrogen source in an actively growing culture causes the organism to produce lignin degrading enzymes at the maximum rate.

Other fungi (e.g., species of Aspergillus and Fusarium) and many bacteria (e.g., species of Norcardia, Bacillus, Streptomyces, Pseudomonas, Flavobacterium, Aeromonas, and Xanthomonas) have been conclusively shown to at least partially degrade lignin. Xanthomonas was shown to attack lignin as the sole source of carbon and energy.

Determining the structure of native lignins and microbial attack mechanisms on lignin are the subjects of current research. Getting to the middle lamella lignin in wood chips would seem to be a significant problem for microorganisms. Electron microscopy[29-31] has shown that the white-rot fungi spreads hyphae through the wood fibers by utilizing the naturally existing connections (e.g., pits). Growth begins in the lumen and spreads outwards. Sometimes the fungus will form its own bore holes. The wild-type white-rot fungus will cause a progressive thinning of the cell wall starting from the lumen and continuing outwards. The cellulase-less mutants, however, do not cause such thinning. A separation between cells within or adjacent to the compound middle lamella has been observed after fungal treatment.

Basic research in microbial lignin degradation has progressed to the point where numerous lignin degrading microorganisms have been isolated. It is only a matter of time before biotechnology researchers successfully clone lignin degrading enzyme DNA segments from these organisms into E. coli to produce a genetically engineered microorganism capable of producing the enzyme at a high rate. One such successful cloning of a lignin degrading enzyme into E. coli has already been reported.[10] Many other successful attempts will probably be reported in the future.

POSSIBLE ROLE OF IPC IN BIOPULPING DEVELOPMENT RESEARCH

IPC should consider the immediate initiation of a modest biopulping research effort in conjunction with its High Yield Pulping project. The research would focus on the pulping of wood chips and/or modification of high yield mechanical, thermomechanical, or chemimechanical pulps using enzyme solutions. The goal of the enzymatic treatments would be to produce a high yield and strength pulp with minimal energy input. Initially IPC would not produce the enzyme solutions in its own laboratories but would purchase or obtain the enzymes (when available) from other research laboratories and high tech bioengineering firms (e.g., Genentech, Genex, Cetus, Biogen, etc.). The enzymes probably would be available in sufficient quantity for research purposes. IPC would be well equipped to perform this type of research.

Once a biopulping research effort was on firm ground, it would be worthwhile to set up facilities where microorganisms are grown in pure culture to generate enzyme solutions that are then used to digest wood chips or treat high yield wood pulp. Microorganisms would be obtained from culture collections or isolated by IPC personnel from appropiate sources. This type of activity

would require the services of a microbiologist and biochemical engineer. IPC would have much of the equipment needed to perform this type of research.

Since biological/enzymatic pulping promises to reduce energy consumption, a possible source of funding of a biological/enzymatic pulping research effort would be the Department of Energy. Substantial funding would be needed to staff and equip a laboratory dedicated to gene splicing techniques. In the long term, however, IPC would be well advised to get into this promising research area.

REFERENCES

1. Stanier, R. Y.; Doudoroff, M.; Adelberg, E. A. The Microbial World, third edition, Prentice-Hall, Englewood Cliffs, N.J., 1970.

2. Kobayashi, Y.; Matsuo, R. Chemical and enzymatic pulping of the decorticated pineapple leaf fiber and some physical properties of its paper, Cellulose Chem. Technol. 11:487-99(1977).

3. Kobayashi, Y.; Matsuo, R. Enzymatic pulps prepared by Mould-producing enzyme preparations and their paper, Cellulose Chem. Technol. 12:177-97 (1978).

4. Kobayashi, Y.; Matsuo, R. Enzymatic pulping of bast fibers by alkaline pectolytic enzymes, Cellulose Chem. Technol. 15:639-47(1981).

5. Kobayashi, Y.; Matsuo, R. Enzymatic pulping of Mitsumata bast by alkaline pectolytic enzymes; effect of conditions on sheet properties, Cellulose Chem. Technol. 15:649-59(1981).

6. Kobayashi, Y.; Matsuo, R.; Komae, K.; Okawa, A.; Ebuchi, E. Alkaline enzymatic pulping of Kozo (Paper Mulberry) bast for Japanese fine papermaking - effects of alkaline presoaking on pulping and paper properties, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 2:102-7(1983).

7. Yoshihara, K.; Kobayashi, Y. Retting of Mitsumata bast by alkalophilic bacillus in papermaking, Agric. Biol. Chem. 46(1):109-17(1982).

8. Mayatt, J. H. "Paper," in industrial enzymology: the applications of enzymes in industry, T. Godfrey and J. Reichelt, editors, The Nature Press, New York, New York (1983).

9. Zaborsky, O. R. Comments on biological delignification, in biological delignification: present status and future directions, Proceedings of a Symposium Sponsored by Weyerhaeuser Company, August 30, 1976:79-90.

10. Anon. Gene cloning speeds lignin degradation, C&EN, Oct. 1,1984:5-6.

11. Eriksson, K.-E. Delignification of wood chips by mutant white-rot fungi, in biological delignification: present status and future directions, Proceedings of a Symposium Sponsored by Weyerhaeuser Company, August 30, 1976:5-30.

12. Eriksson, K.-E.; Vallander, L. Biomechanical pulping, Chap. 14 in lignin biodegradation: microbiology, chemistry, and potential applications, T. Kirk, T. Higuchi, and H-m Chang, editors, Vol. II, CRC Press, Boca Raton, Florida, 1980:213-24.

13. Samuelsson, L.; Mjoberg, P. J.; Hartler, N.; Vallander, L.; Eriksson, K.-E. Influence of fungal treatment on the strength versus energy relationship in mechanical pulping, Svensk Papperstid. 83(8):221-25(1980).

14. Eriksson, K.-E.; Vallander, L. Properties of pulps from thermomechanical pulping of chips pretreated with fungi, Svensk Papperstid. 85(6):R33-8 (1982).

15. Eriksson, K.-E. Swedish developments in biotechnology based on lignocellulosic materials, Advances in Biochemical Engineering, 20:193-204(1981).

16. Kirk, T. K. Biodelignification research at the U.S. Forest Products laboratory, in biological delignification: present status and future directions, Proceedings of a Symposium Sponsored by Weyerhaeuser Company, August 30, 1976:31-54.

17. Kirk, T. K.; Chang, H.-M. Potential applications of bio-liginolytic systems, enzyme and microbial technology, 3(3):189-96(1981).

18. Bar-Lev, S. S.; Kirk, T. K.; Chang, H.-M. Fungal treatments can reduce energy requirements for secondary refining of TMP, Tappi J. 65(10):111-13 (Oct. 1982).

19. Kirk, T. K.; Jeffries, T. W.; Leatham, G. F. Biotechnology: applications and implications for the pulp and paper industry, Tappi J. 66(5):45-51 (May 1983).

20. Kirk, T. K. Pulping and bleaching with delignifying enzymes, Pima Mag., Dec. 1983:44-5.

21. Fukuzumi, T. Biological pulping: fundamental principles and technological problems, Japan Tappi 34(12):761-8(Dec. 1980).

22. Pilon, L.; Desrochers, M.; Jurasek, L.; Neumann, P. J. Increasing water retention of mechanical pulp by biological treatments, Proceedings of the 1981 Tappi Annual Meeting, March, 1981:293-7.

23. Pilon, L.; Desrochers, M.; Jurasek, L.; Neumann, P. J. Increasing water retention of mechanical pulp by biological treatments, Tappi J. 65(6):93-6 (June 1982).

24. Abson, D., editor, Biological delignification: p esent status and future directions, Proceedings of a Symposium Sponsored by Weyerhaeuser Company, (August 30, 1976).

25. Kirk, T.; Higuchi, T.; Chang, H.-M., editors, Lignin biodegradation: microbiology, chemistry, and potential applications, Vol. I and II, CRC Press, Boca Raton, Florida (1980).

26. Crawford, D. L.; Crawford, R. L. Microbial degradation of lignin, enzyme and microbial Tech., 2(1):11-22(1980).

27. Ander, P.; Eriksson, K.-E. Influence of carbohydrates on lignin degradation by the white-rot fungus sporotrichum Pulverultum. Svensk Papperstid. 78(18):643-52(1975).

28. Eriksson, K.-E.; Grunewald, A.; Vallander, L. Studies of growth conditions in wood for three white-rot fungi and their cellulaseless mutants, Biotech. and Bioeng. 22:363-76(1980).

29. Eriksson, K.-E.; Grunewald, A.; Nilsson, T.; Vallander, L. A scanning electron microscopy study of the growth and attack on wood by three white-rot fungi and their cellulase-less mutants, Holzforschung 34(6): 207-13(1980).

30. Ruel, K.; Barnoud, F.; Eriksson, K.-E. Micromorphological and ultrastructural aspects of spruce wood degradation by wild-type sporotrichum pulverulentum and its cellulase-less mutant cel 44, Holzforschung 35(4): 157-71(1981).

31. Ruel, K.; Barnoud, F.; Eriksson, K.-E. Ultrastructural aspects of wood degradation by sporotrichum pulverulentum, Holzforschung 38(2):61-8(1984).

32. Kirk, T. K. What have studies of model compounds revealed about the fungal degradation of lignin, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 3:7-12(1983).

33. Chen, C.-L.; Tai, D.; Terazawa, M.; Chang, H.-M.; and Kirk, T. K. Chemistry of birch lignin biodegradation by Phanerochaete chrysosporium, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 3:13-18(1983).

34. Palmer, J. M.; Evans, C. S. Extracellular enzymes produced by Coriolus versicolor in relationship to the degradation of lignin, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 3:19-24(1983).

35. Fukuzumi, T. Enzymatic hydrolysis products from lignin or lignin-carbohydrate in wood, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 4:140-3(1983).

36. Tai, D.; Terazawa, M.; Chen, C.-L.; Chang, H.-M.; Kirk, T. K. Characterization of biodegraded lignins isolated from birch wood decayed by Phanerochaete chrysosporium by ^{13}C NMR spectroscopy, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 4:144-9(1983).

37. Terazawa, M.; Tai, D.; Chen, C.-L.; Chang, H.-M.; Kirk, T. K. Identification of the constituents of low molecular weight fraction obtained from birch wood degraded by Phanerochaete chrysosporium, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 4:150-5(1983).

38. Hiroi, T.; Tamai, A. Degradation of wood components by white-rot fungi, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 4:156-60(1983).

39. Onderka-Leclair, E.; Cyr, N. Degradation of wood components in aspen poplar by fomes igniarius, white-rot fungi, 1983 International Symposium on Wood and Pulping Chemistry, Japan Paper Association (sponsor), 4:161-4 (1983).

40. Bass, A. B. Managing for success: the genentech story, Technology Review, 88(4):28-9(May/June 1985).